THE
RISE AND DEVELOPMENT
OF
ORGANIC CHEMISTRY

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THE

RISE AND DEVELOPMENT

OF

ORGANIC CHEMISTRY.

BY

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HERMANN KOPP,

THE GREAT HISTORIAN OF CHEMISTRY.

THE RISE AND DEVELOPMENT OF ORGANIC CHEMISTRY.

CHAPTER I.

Chemical Knowledge of the Ancients.—Origin of the Word Chemistry.—Alchemy.—Iatrochemistry.—First Attempts to Classify Chemical Substances.—Distinction between Inorganic and Organic Bodies; Lemery.—The Period of Phlogistic Chemistry. Becher; Stahl; Scheele.—The Beginning of Quantitative Chemistry. Lavoisier; Berzelius; Gmelin.—The Ætherin Theory.

Organic Chemistry as a science has been created almost entirely during the present century; nevertheless many facts of universal importance for chemistry generally were first observed in the case of organic bodies.

Thus, the only *acid* known to the ancients was vinegar or dilute acetic acid; hence its name and the conception of acidity were expressed by closely related words (*ὄξος*, *acetus*, vinegar; *ὀξύς*, *acidus*, sour). By the action of vinegar on the alkalis the first *artificial salts* were obtained; the first *reagent* which we find mentioned is an infusion of nut-galls; Pliny tells us that paper steeped in it was used for the detection of green vitriol (*atramentum sutorium*) in verdigris, as in case of such an adulteration the paper would be blackened on placing the suspected substance on it: "*Deprehenditur et papyro, galla prius macerato; nigrescit enim statim ærugine illita.*" The same reagent, as well as the juice of the pomegranate was employed for recognising a kind of alum used for the dyeing of black; this was either native green vitriol or a mineral containing it.

A crude method of *distillation* was also early known and used for obtaining oil of turpentine. The Gauls and Germans understood the art of *soapmaking*, and thus introduced into Rome a process, by the exact study of which in our days much light has been thrown on an important part of organic chemistry.

The *fermentation* of grape-juice was known to prehistoric nations, and the art of brewing beer to the Egyptians, Gauls, Germans, and others.

Organic dyes were already skilfully employed in India, Phœnicia, and Egypt; besides these the ancients were acquainted with many other organic bodies, such as oils, various fats, sugar, gums, resins, starch, &c., as well as with a number of inorganic substances.

Chemistry as a science was however unknown to them; it has been stated, and I shared this belief for some time, that those of their philosophers who desired to promote scientific knowledge followed the treacherous path of speculation, instead of the safe way of observation and experiment; but I think this statement is not quite correct, as we find amongst the ancients very many keen observers. Even Herakleitos had a clearer idea of the inseparable connection between matter and motion than many modern physicists. It is obvious that a new science is not created all at once, springing forth completely armed like Minerva from the head of Jupiter, or in all its beauty like Venus from the froth of the sea. Chemistry as a science of atoms is an offspring of Physic, the science of molecules, and this again is founded on the science of masses, or Mechanic. These two sciences had therefore to be developed to some extent ere the chemical facts then known could be considered from a common standpoint, and chemistry in its crudest shape make its appearance.

Chemistry as a science (*scientia chimiœ*) is first mentioned by Julius Maternus Firmicus, who in the first half of the fourth century wrote a book on Astrology, commonly known by the name of *Mathesis*, but he does not explain the meaning of it.* However another writer, who probably lived at the same time, if not earlier, gives us an explanation. Zosimus the Panopolite, according to Georgios Synkellos, a writer of the ninth century, states that χημεία (or χυμεία, as some manuscripts have) meant the art of making gold and silver, and in the same sense it is used by other Greek writers.† All these having been in close connection with the university of Alexandria, it has been inferred that the artificial preparation of the noble metals was first attempted in Egypt.

That country was conquered by the Arabians in 640. Here they made their first acquaintance with chemical science; they prefixed their article to its Greek name and thus introduced the terms: Alchymy, Alchimy, or Alchemy.

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* Kopp, Beiträge zur Geschichte der Chemie I., 43.

† Ibid. 9 and 54.

The origin and meaning of these terms has often been discussed. Plutarch states that the old name of Egypt was *χημία*; that it was so called on account of its black soil, and that the same word designated the black of the eye, as the symbol of darkness and mystery. From this the conclusion has been drawn, that chemistry originally meant the science of Egypt, or perhaps the secret or black art. But alchemy has never been called the black art, a name which was exclusively reserved for magic or necromancy.

Others believe the word was derived from *χυμός*, juice or liquid. To this it has been objected that the original spelling was *χημεία* and not *χυμεία*, which, although H. Kopp inclines to this view, has not yet been proved satisfactorily. Humboldt believes that the latter word got into some manuscripts by a mistake of the transcriber, and continues: "Alchimy commenced with the metals and their oxides, and not with the juices of plants." This objection, however, cannot be maintained at all, because vegetable juices or, at least, substances designated by their names, are mentioned by the older alchemists as the most potent substances by which transmutations could he effected.*

Professor Gildemeister† has, a short time ago, published an interesting paper on this subject, in which he maintains the derivation of the word chemistry from *χυμός*. According to him *kîmiyâ* in Arabic does not originally have an abstract meaning, and is the name, not of a science, but of a body by which, or rather by a substance obtained from which, the transmutation of metals is effected; it is synonymous with *iksîr*. Alchemy as a science was called: The preparation of *kîmiyâ* or *iksîr*, also the science of the preparation of *kîmiyâ* or, more shortly, science of *kîmiyâ*. In the Arabic Lexicon (Qâmûs) *al-iksîr* is explained by *al-kîmiyâ*, and the latter again by the former, or by any medium which, applied to a metal, transports it into the sphere of the sun or the moon, *i.e.*, converts it into gold or silver.

Even to this day the word is used in the concrete sense; Kotschy‡ relates that the pasha of Nicosia talked much of flowers, chiefly *kimia*, a plant having the property of converting metals into gold.

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* Kopp. loc. cit. 76.

† Zeitsch. deutsch. morgenländ. Ges. XXX., 634.

‡ Petermann Geog. Mitth. VIII. 294.

The later Arabic writers, however, called the science shortly *al-kîmiyâ* and retained the term *al-iksîr* (elixir) for the transmuting medium or the philosopher's stone. This latter word is identical with *ξήριον*, as the writers of the Alexandrine school called the philosopher's stone,* while the same name was employed by the physicians for a healing powder, used for sprinkling over wounds, *i.e.*, a desiccative powder (from *ξηρός*, dry).†

Now the correlate to dry is moist or liquid, *χύμος*, and from this is derived *χυμεία*, a moist substance, corresponding to *λιθεία*, a material formed of *λίθος*, or *κεραμεία*, the occupation with *κέραμος*.

Ibn Khaldûn, who lived in the 14th century, says that from the philosopher's stone a liquid or a powder might be prepared called *iksîr*, which, when thrown on molten copper converted it into silver, and molten silver into gold. In opposition to its etymology the word is here used for a liquid, because at that time *kîmiyâ* no longer meant the transmuting substance, but the science of transmutation, and explains why to-day we may understand by elixir a liquid.

During the period of alchemy the study of inorganic substances made more progress than that of organic bodies. The improved methods of distillation led, however, to the discovery of different essential oils and of alcohol, which was considered as one of the substances from which the philosopher's stone could be prepared, and, at the same time, as a most potent medicine. It was therefore called *aqua vitæ*, and Raymund Lully, who describes several methods of obtaining it as strong as possible, says that it would make old people young again, and was *consolatio ultima corporis humani.*

Lully examined the action of sulphuric acid on alcohol, and described it in his *Epistola accurtationis lapidis benedicti*, addressed to Robert Bruce. He knew besides the violent action of nitric acid on spirits of wine, from which some have inferred that he was acquainted with ether and sweet spirit of nitre, which, however, is very doubtful.‡

Up to the 16th century the principal object of chemical investigation had been the endeavour to find the philosopher's stone. But now chemistry began to develop itself in two new and different paths, opened by two distinguished men: Agricola, the father of Metallurgy, and Paracelsus, the founder of Iatrochemistry. It might have been expected that, by the work of the latter and of other eminent medical chemists, the knowledge of organic chemistry would have made great progress. But this was not the case, because the Iatrochemists, in opposition to the school of Galen and Avicenna, employed as medicines chiefly metallic preparations, and only a few endeavoured to extract from organic bodies their active medical principles. Thus succinic acid, benzoic acid, pyroligneous acid, and sugar of milk were discovered.

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* Kopp. loc. cit. 209.

† Zosimus calls the substance by which copper is tinged yellow or converted into brass: *τὸ διὰ τῆς θουθίας ξήριον*, a powder prepared by means of tutia; now tutia (zinc oxide) is still to-day used in medicine as a desiccative!

‡ Kopp, Geschichte der Chemie, IV., 299.

A new era in the history of chemistry begins with Robert Boyle, who first clearly pointed out that chemistry must no longer be the handmaid of the alchemist or physician, that it was a science *sui generis*, an autonomous and essential branch of the great study of nature.

Boyle was also the first chemist who clearly grasped the idea of the distinction between elements and compound bodies, and thus enabled chemists to ascertain the composition of bodies by the methods of analysis and synthesis. But this only in the case of inorganic bodies, the methods then in use being not applicable to substances formed in organic nature.

Just at the beginning of the new era we find for the first time a sharp distinction made between inorganic and organic bodies. Hitherto they were classified according to their physical properties, and many terms still in practical use remind us of that time.

Oil of olives and other fatty oils were classed together with oil of vitriol and oil of tartar (deliquesced potasses); spirit of wine was placed into the same category as stannic chloride (*spiritus fumans Libavii*), ammonia (*spiritus cornu cervi*), ammonium sulphide (*spiritus fumans Boylei*), nitric acid (*spiritus nitri fumans Glauberi*), and hydrochloric acid (*spiritus salis Glauberianus*). Chlorides having a soft consistency were called butters, and consequently cow's butter figured alongside of butter of zinc and butter of antimony. Colourless solids soluble in water and having a peculiar taste were from Pliny's time called salts, and sugar was therefore included in this class, while the soluble coloured salts of the heavy metals were known as vitriols.

In 1675 Nicolas Lemery published his celebrated *Cours de Chymie*, which during the lifetime of the author went through thirteen editions, and appeared even as late as 1756, naturally in a completely revised edition. It was considered as the best text-book of chemistry, and was translated into Latin, English (Professor Black recommended it in his lectures), German, Italian, and Spanish.

According to Lemery the object of chemistry is to investigate the different bodies "*qui se rencontrent dans un mixte.*" By the last word he understood natural products in general. He divided them into three classes: — mineral, vegetable, and animal bodies.

To the first belong the metals, minerals, earths, and stones; in the second he classes plants, resins, gums, fungi, fruits, seeds, juices, flowers, mosses, manna, and honey; and the third includes animals, their different parts and excrements.

His classification was therefore only based on the origin of the different substances, and became faulty as he tried to be too consistent. Thus, amber and the products of its dry distillation he describes in the first or mineral part, while tartar and other potassium salts are classed among the vegetable substances. So again is acetic acid, but the acetates and the products formed by their dry distillation are treated in the first section. In the third part he speaks only of the distillation of vipers, of urine, wax, and honey, which he has mentioned already in the section treating of vegetable bodies.

Lemery's classification having been soon generally accepted, the founders of the phlogiston theory endeavoured to develop it and to justify a classification, founded on the origin of chemical substances, from a chemical point of view exclusively. Becher had already said in his *Physica subterranea*, 1669: "The elements occurring in the three natural kingdoms are the same, but they are combined in mineral bodies in a manner more simple than they are in vegetable and animal substances."

Stahl in his *Specimen Becherianum*, 1702, is of opinion that in minerals the earthy principle predominated, while organic bodies contained more of the aqueous and combustible principle (phlogiston). Both make their appearance when an organic body is heated in the absence of air or subjected to dry distillation, water being formed and charcoal left behind.

This definition of organic chemistry by Stahl is as admirable as that of chemistry in general: "*Chemia, alias Alchymia et Spagirica,** *est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi.*"

In the first hand-books of phlogistic chemistry we find the compounds which are now called organic bodies classed among other combustible substances. Sulphur, the different kinds of coal, bitumen, resins, oils, fats, camphor, &c., formed a common group. It was assumed by some that these bodies differed from mineral substances by containing a peculiar oil, which was rich in phlogiston.

Neither theoretically nor practically did organic chemistry make much advance up to the end of the phlogistic period. When organic bodies were examined it was for the object of pharmacy or the improvement of technical processes such as dyeing, &c.

However, at the end of the last century chemists began to investigate organic substances from a purely scientific point of view; among these chiefly Scheele, who discovered or first clearly distinguished the most important organic acids. He proved that the acid of grapes is quite different from that contained in lemons, that another existed in apples, and again a new one was found in sorrel. The latter he obtained artificially by the oxidation of sugar, and found that it was not identical with the one which is produced in the same way from sugar of milk. He discovered gallic acid in nut-galls, lactic acid in sour milk, and uric acid in urine.

To prepare some of these acids in the pure state, he devised methods which are still in use. Before him only succinic and benzoic acids were better known, both being obtained by means of sublimation from amber and gum benzoïn. He showed that the latter acid forms a lime salt freely soluble in cold water, which dissolves the free acid but sparingly. The latter may therefore readily be obtained by boiling gum benzoïn with milk of lime, concentrating the filtrate and precipitating from it the benzoic acid by the addition of hydrochloric acid.

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* According to Prantl (Kopp, loc. cit. 64) the origin of this word is based on Plato's views on separating (σπάω) and uniting (ἀγείρω), but it is not found in the writings of any alchemist before the 15th century. Libavius at the beginning of the 17th century gives the same derivation as Prantl, and says that it was recently introduced into the science.

On the other hand he found that tartaric, citric, and malic acids form with lime or oxide of lead insoluble salts, by means of which these acids may be separated from other substances present in the fruit, and the pure acids obtained by decomposing the lime or lead salt with sulphuric acid.

He further showed that oils and fats contain a common constituent, *the sweet principle of oils* (glycerin), and pointed out that it must be closely related to sugar, not only on account of its sweet taste, but also because it yields, like the latter, oxalic acid by heating with nitric acid.

His friend Bergman worked in a similar direction, while Rouelle studied animal chemistry, which had hitherto been completely neglected, and discovered, among other substances, urea and hippuric acid.

Such researches gave a great impulse to the study of organic compounds, and Lavoisier, having once found the true explanation of the process of combustion, analysed a number of organic bodies. He came to the conclusion that vegetable substances consisted commonly of carbon, hydrogen, and oxygen, while those formed in the animal organism contained, in addition to these three elements, mostly nitrogen, and sometimes also sulphur and phosphorus.

Lavoisier's chemistry was essentially the chemistry of oxygen and its compounds; consequently on examining a body he endeavoured to find out whether it could be combined with this element or whether it contained it already. That portion of a compound which is combined with oxygen was called *la base* or *le radical.* The latter term was first used by his friend Guyton de Morveau,* who, after speaking of the acids of nitrogen, carbon, sulphur, and phosphorus, goes on to discuss the nomenclature of acids of unknown composition, such as muriatic acid, boracic acid, the acid of vinegar, &c., with regard to which he says: "*Nous nous sommes contentés de désigner l'être simple qui y modifie l'oxigène par l'expression de* BASE ACIDIFIABLE, *ou, pour abréger, de* RADICAL *de tel acide; afin de garder la même analogie, et de pouvoir considérer à leur tour chacun de ces êtres d'une manière abstraite.*"

Lavoisier extended these views; a radical could be a simple or compound body, and thus he says: "*le carbone est le radical*

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* Mémoire sur le Développement des Principes de la Nomenclature méthodique, 1787.

de l'acide carbonique," while vegetable acids contain "*le radical oxalique, tartarique, &c.*"

The difference between inorganic and organic compounds he defines as follows*:—

"*J'ai déjà fait observer, que dans le règne minéral presque tous les radicaux oxidables et acidifiables étaient simples; que dans le règne végétal au contraire et surtout dans le règne animal, il n'en existait presque pas qui ne fussent composés au moins de deux substances, d'hydrogène et de carbone; que souvent l'azote et le phosphore s'y réunissaient, et qu'il en résultait des radicaux à quatre bases.*"

Lavoisier observed that a simple body could form more than one oxide, and from this he concluded that organic radicals behaved in the same way; he therefore considered sugar as the neutral oxide "*d'un radical hydro-carboneux,*" and oxalic acid as its higher oxide. He went even so far as to suggest that the oils which he believed to be hydrocarbons might actually constitute organic radicals in the free state, which by oxidation could be converted into neutral oxides and vegetable acids.

Of his different researches on the field of organic chemistry, which however he did not treat as a separate study, his investigations of the process of fermentation must be mentioned, not so much because he first showed that sugar is thus resolved into alcohol and carbon dioxide, but because he clearly understood the importance of this investigation, and showed that such a chemical change can be expressed by an equation which may be controlled by analysis, inasmuch as the weight of the original substance, as well as that of each of the elements contained in it, must be found again in the products.

Lavoisier did not strictly separate the inorganic compounds from organic bodies; thus, he grouped all the acids together and subdivided them into mineral, vegetable, and animal acids. His next followers did the same with a few exceptions; thus, in Gren's Natural Philosophy, published at the end of the last century, we find the organic compounds treated in a separate chapter; they are defined as the compounds existing in the vegetable and animal organism, composed of a limited number of elements, produced in the living body only, and not capable of being prepared artificially.

When however it was found that many compounds occur both in the vegetable and animal kingdom, a strict distinction between inorganic and organic chemistry, as we have it now, was generally accepted.

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* Traité élémentaire de Chimie, 1793, I., 209.

For a long time however uncertainty and difference of opinion prevailed as to the boundary line of the two. One reason was that mineral bodies, as well as a few found in the organic world, gave on analysis numbers showing clearly that the composition was in accordance with the laws of constant and multiple proportions, while the majority of organic bodies gave analytical results showing that they had a very complicated composition which seemed not to be based on the above laws.

Berzelius says, in 1811, that he intended therefore to analyse a number of them carefully in order to decide this question. He improved the methods of organic analysis, and the results obtained clearly showed that although most organic bodies have a much more complicated composition than mineral compounds, yet they can be expressed by atomistic formulæ.

In taking up again the views of Lavoisier, he says: "After we have got a clearer insight into the difference existing between the products of organic and inorganic nature and the different manner in which the ultimate components are united with each other, we find this difference consists really in the fact that in unorganic nature all oxidised bodies contain a *simple radical,* while all organic substances are *oxides of compound radicals.* The radicals of vegetable substances consist generally of carbon and hydrogen, and those of animal substances of carbon, hydrogen, and nitrogen."*

These ideas he did not, however, develop at that time, nor did he enter on any discussion of these hypothetical organic radicals, although an excellent example of a compound radical had then become known by Gay-Lussac's discovery of cyanogen.

However, most chemists regarded the cyanogen compounds as belonging to inorganic chemistry. Thus a boundary line was still wanting, and L. Gmelin, in his hand-book of theoretical chemistry, 1817, said that although inorganic and organic compounds must be kept strictly separate, the difference between them could be more easily felt than defined. As a chracteristic for the former he regards their binary constitution; the most simple consist of only two elements, such as a basic oxide and an acid oxide, which by combining form again a binary compound of a higher order, &c.

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* Lehrbuch, 2nd ed., 1817, I. 544.

The most simple organic bodies are, according to Gmelin, at least ternary compounds, or made up of three elements; and moreover their elements are not combined in such simple proportions of their atomic weights as inorganic substances. Consequently he describes marsh gas, olefiant gas, cyanogen, &c., in the inorganic part. A marked difference between inorganic and organic bodies he found also in the fact that the former can be prepared artificially from their elements, but not the latter.

Another view held at that time by many chemists had, in some respect, a resemblance with that of Stahl, according to which organic bodies contained an aqueous and a combustible principle. Lavoisier himself, in the account of his researches on fermentation, states that it was only with difficulty he got rid of this conception, and began to consider sugar, not as a compound of carbon and water, but of carbon with hydrogen and oxygen.

In 1815 Gay-Lussac found the specific gravity of alcohol vapour to be equal to the sum of that of aqueous vapour and olefiant gas, and the specific gravity of ether equal to that of aqueous vapour plus twice that of olefiant gas; and therefore it might be assumed that water and olefiant gas were the components of alcohol and ether. In the next year Robiquet and Colin found that hydrochloric ether (ethyl chloride), which is formed by the action of hydrochloric acid on alcohol, could be regarded as a compound of this acid with olefiant gas. These views were extended by Dumas and Boullay,* who showed that many other derivatives of alcohol might be viewed in a similar way as compounds of olefiant gas and other groups of atoms, and therefore be compared with those of ammonia. The following table is taken from their memoir, the formulæ being however expressed by the atomic weights now in use.

Hydrochloric Ether	C_2H_4, HCl	Ammonia hydrochloride	NH_3, HCl
Hydriodic ether	C_2H_4, HI	Ammonia hydriodide	NH_3, HI
Nitrous ether	C_2H_4, HNO_2	Ammonia nitrite	NH_3, HNO_2
Sulphovinic acid	C_2H_4, H_2SO_4	Acid Ammonia Sulphate	NH_3, H_2SO_4
Alcohol	C_2H_4, H_2O	Aqueous Ammonia	NH_3, H_2O
Ether	$(C_2H_4)_2, H_2O$		

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* Ann. Chim. Phys., 37, 15.

These views they extended not only to other derivatives of alcohol, but also to other compounds, such as grape-sugar, which being resolved by fermentation into alcohol and carbonic acid, was regarded as a compound having a constitution analogous to bicarbonate of ammonia:

Grape-sugar..................	C_2H_4, CO_2, H_2O.
Ammonia bicarbonate......	NH_3, CO_2, H_2O.

Berzelius at first opposed this theory, but afterwards accepted it, and called the group C_2H_4 *Ætherin*; yet although we find here for the first time a large number of organic bodies considered from a common point of view, the ætherin theory was not generally accepted, and no attempt was made to extend it to other groups of organic bodies, which at that stage of development of the science would have been scarcely possible.

Besides, it was opposed by various facts; thus olefiant gas and ether could be obtained by taking water out of alcohol, but the inverse reaction could not be effected, and no methods were known for obtaining any other compound of ætherin by the direct combination of their supposed components, as is the case with the ammonia compounds.

CHAPTER II.

BELIEF IN A SO-CALLED VITAL FORCE.—THE FIRST ARTIFICIAL PRODUCTION OF AN ORGANIC COMPOUND.—ORGANIC RADICALS.—THE THEORY OF SUBSTITUTION. DUMAS, LAURENT; BERZELIUS' OPPOSITION.—NUCLEUS THEORY.

As already stated L. Gmelin found a characteristic difference between inorganic and organic compounds in the fact that the latter cannot be prepared synthetically from the elements like the former. This view was taken up again by Berzelius, who, 1827, in his treatise says: "that the elements present in living bodies obeyed laws totally different from those which rule inanimate nature." It was at that time supposed that the compounds which are formed in plants and animals were produced under the influence of a so-called vital force, and could therefore not be prepared artificially. It was believed that organic bodies might be converted by chemical processes into other organic compounds, but that it was impossible to produce any such body by synthesis. Thus grape-sugar is an organic body widely distributed in the vegetable kingdom; by fermentation it yields alcohol, which can readily be transformed into ether, acetic acid, and many other compounds, all of which, as they could not be prepared by any synthetical method, were classed among organic compounds.

But as early as 1828 Wöhler made the most important discovery that cyanate of ammonia, which then was regarded as an inorganic compound, is most readily converted into urea. Thus for the first time a body hitherto produced in the living organism of animals only was obtained artificially; but this synthesis was incomplete, inasmuch as at this time no method was known to obtain cyanogen compounds directly from their constituent elements.

Moreover this synthesis remained an isolated fact for many years, and did not shake the belief in a mysterious vital force. It was then maintained that urea as an excretion of the animal organism, and a compound which most readily is resolved into carbonic acid and ammonia, formed a connecting link between inorganic and organic compounds, which was just standing on the boundary line, and that such bodies might be prepared in the laboratory, but not those of more complicated constitution.

The belief in a vital force has disappeared years ago; to-day we know that the same chemical laws rule animate and inanimate nature, and that any definite compound produced in the former can be prepared by synthesis as soon as its chemical constitution has been made out.

When, 1832, Wöhler and Liebig* published their classical investigation, "Researches on the Radical of Benzoic Acid," Berzelius declared that a new day had commenced in organic chemistry, because they clearly proved that oil of bitter almonds, benzoic acid, which is easily obtained by the oxidation of this oil, and a host of other compounds which can be obtained from them by very simple reactions, have, as a common centre, a group of atoms, C_7H_5O, which might be regarded as a "compound element," and which they called *Benzoyl* (the ending being derived from ὑλη, stuff or matter). A compound radical containing oxygen! We can hardly to-day imagine what a revolution this produced in the chemical world; oxygen, which since Lavoisier's time had been the supreme ruler, was thus deprived of its glory, and had to take its place among the rank and file of the other simple substances.

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* Ann. Pharm. III., 249.

Berzelius, who in 1817 regarded organic compounds containing oxygen as oxides of compound radicals, consisting of hydrogen and carbon, and sometimes also of nitrogen, greeted the new radical with such joy that he proposed to call it *Proïn* (from πρωΐ, in the beginning of the day, in the sense of ἀπὸ πρωΐ ἕως ἑσπερας, Act. 28, v. 23), or Orthrin (ὀρθρὸς, dawn of the morning).*

The theory of organic radicals was next further developed by Berzelius and Liebig, who opposed the views of Dumas and Boullay, that alcohol and its derivatives contained olefiant gas as a proximate constituent, but their views did not always agree. Thus, Berzelius considered alcohol and ether as oxides of two different radicals, while Liebig, in a memoir which forms the foundation stone of the theory of compound radicals, as generally adopted afterwards, showed that both compounds contained the same radical, which he called *Ethyl*, ether being its oxide and alcohol a hydrate of the latter.† Hydrochloric and hydriodic ether, sulphovinic acids, were now regarded as a kind of salts of ethyl, which, similar to its oxide and hydrate, could be compared with the corresponding compounds of potassium. In the same way other alcohols were assumed to be hydrated oxides of compound hydrocarbon-radicals. Liebig went even as far as to prognosticate the possible isolation of these hypothetical bodies, which might perhaps be effected by the action of potassium on their iodides or chlorides.

Oxidation converts the alcohols in monobasic acids; methyl alcohol CH_4O, or wood-spirits yields formic acid CH_2O_2, and ethyl alcohol C_2H_6O, or spirits of wine, acetic acid $C_2H_4O_2$. According to Liebig these bodies had a constitution analogous to benzoic acid; they contained the radicals CHO and C_2H_3O.

* Ann. Pharm. III., 282.

† Ann. Pharm. IX. 1.—Dr. Robert Kane, as far back as 1833, published a paper (Dublin Journ. Med. Chem. Science, II. 348), stating that, just as according to the ammonium theory of Berzelius, the addition of one atom of hydrogen to ammonia converts it into a substance possessing many properties in common with the metals, it might be assumed that the compounds of ætherin contained a group consisting of olefiant gas (or an isomeric body) plus hydrogen, and for which he proposed the name *æthereum*. His paper however became very little known beyond Dublin. He says himself that his speculations were a subject of amusement and ridicule among the chemical circles of this city. Liebig was certainly not influenced by it, and it was only after his views had been generally accepted that Kane brought forward his claims.—(Phil. Mag. XIV., 163.)

This view was opposed by Berzelius, who already in 1833 had remarked that benzoyl C_7H_5O, although it behaved just like a simple body, was really an oxide of a compound radical, and could like other lower oxides combine with more oxygen to form an acid. The true radical of formic acid therefore ought to be formyl CH, and that contained in acetic acid acetyl C_2H_3. Liebig agreed to these views, because they allowed the grouping of a certain number of compounds round a common centre.

Thus Regnault found, 1835, that by the action of alcoholic potash on Dutch liquid (ethene dichloride) $C_2H_4Cl_2$, a compound having the composition C_2H_3Cl was formed, and Liebig discovered at the same time aldehyde C_2H_4O, which on oxidation is readily converted into acetic acid. Regnault's compound was now regarded as acetyl chloride, which could combine with hydrochloric acid, forming ethene dichloride, whilst aldehyde and acetic acid were believed to be hydrates of two different acetyl oxides.*

Chloroform, $CHCl_3$, which Liebig also discovered, now appeared as a trichloride of formyl, and in proof of this view it was shown that by the action of alkalis it is transformed into formic acid, and that consequently between these two compounds similar relations exist as between phosphorus trichloride and phosphorous acid.

Dumas, who had an interview with Liebig in 1837, was converted by him to his views; in a paper published in Liebig's and his name† he says that nature formed from a small number of simple bodies the large host of organic compounds; the former combining in the first instance to radicals behaving analogous, partly to chlorine or oxygen, partly the metals.

The true elements of organic chemistry consisted of such radicals as, for instance, cyanogen, benzoyl, ethyl, &c., and not of the simple bodies, which could be isolated from the compounds of these radicals only by completely annihilating their organic nature.

Dumas then stated that Liebig and he had set themselves the task to discover such radicals, and hoped to solve the problem with the aid of younger chemists.

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* At that time the equivalent formulæ were generally used ($C=6$, $O=8$, $H=1$) and the above compounds written C_4H_3Cl, C_4H_3O+HO, $C_4H_3O_3+HO$.

† Compt. rend. V., 567.

The new day in organic chemistry which Berzelius had predicted appeared thus to proceed peacefully; yet already threatening clouds had gathered near the horizon, and a violent storm soon broke out.

While Berzelius and Liebig remained faithful to their theories, and the latter defined organic chemistry as "*the chemistry of compound radicals*,"* Dumas arrived at conceptions which appeared to him to be incompatible with the radical theory. This theory, in its fundamental views, was strictly dualistic, like inorganic chemistry, the only difference being the assumption that in organic chemistry compound radicals played a similar part as the elements in mineral chemistry. Liebig,† on discussing this question in 1838, says:

"In the history of the evolution of any science the researches of the time being furnish certain general relations, which every moment are altered and improved by new discoveries; thus an endeavour arises to arrange the newly-discovered facts and to find the common bond by which they are linked together. Our theories are an expression of the views of the period; only facts are truths, while the explanation of their causal connection approaches truth more or less closely."

"The foundation of any view in regard to the constitution of a compound is, as self-evident, a positive knowledge of the proportions, by weight, in which the different elements are combined together, and above all we must know how much of each element a certain body contains."

"The variation in the composition of two or more bodies of different properties is however in many cases so small, and the errors of our analytical method are so great, that analysis does not always give us a clue to the number of atoms contained in a compound. For this reason a perfectly new method of investigation had to be created, which in inorganic chemistry is rarely employed; we are obliged to combine the body with another of known composition, or to resolve it into two, three, or more products, and if the quantities and composition of these bear a direct relation to the weight and composition of the substance from which they have been obtained, any doubt about the composition of the latter comes to an end. We follow therefore the course of the mathematician, and try to determine or to represent an unknown quantity by equations."

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* Handb. org. chem. 1843, 1.

† Ann. Pharm. XXV., 1.

"But the equations thus obtained give in a few cases only a clue to the mode in which the elements are combined together. The behaviour of inorganic compounds on the other hand gives us definite and unerring rules for conclusions of this kind. We submit therefore the (organic) body to certain changes similar to those which analogous inorganic compounds undergo under the same conditions, and if it behaves in a similar way, we come to the conclusion that it has a similar constitution, or *vice versa.* We compare therefore the compounds which an organic body forms, if they possess properties belonging to a known substance, with the composition and the deportment of the latter. Thus we have been led to the idea of certain compound bodies, which remain unchanged in a series of combinations, which may be replaced by a simple body or form with it compounds, in which the latter can be replaced by other elements; consequently bodies, which in their compounds occupy the place of simple substances, play the part of elements."

"We therefore consider cyanogen as a radical, because it is (1) the never-varying constituent of a series of compounds; because it can (2) be replaced in these by other simple bodies; and because (3) in its combinations with a simple body this latter can be separated or replaced by equivalents of other simple bodies."

"Of these three chief characteristics of a compound radical, two at least must be fulfilled ere it can really be regarded as a compound radical."

Liebig's classical definition of a compound radical holds good to this day.

The radical theory was strictly dualistic and electro-chemical; consequently in the same way as oxygen and the halogens were called electro-negative, and hydrogen and the metals electro-positive elements, so the radicals were also divided into negative ones, or such forming acids, and positive ones, forming basic oxides.

This theory, of which Berzelius was the founder, encountered great difficulties in explaining certain facts, chiefly discovered by French chemists, who by the action of chlorine on organic bodies obtained a series of remarkable compounds.

As early as 1815 Gay-Lussac had observed that by the action of chlorine on prussic acid it is converted into chloride of cyanogen, its hydrogen being completely replaced by this element. Afterwards he found that beeswax bleached by means of chlorine loses hydrogen, and at the same time takes up a volume of chlorine quite equal to that of the hydrogen removed.* Faraday found, 1821, that ethene dichloride (Dutch liquid) $C_2H_4Cl_2$ by the continued action of chlorine is converted into the so-called carbon sesquichloride C_2Cl_6, and pointed out that in this case chlorine is replaced by hydrogen volume for volume. In their researches on the benzoyl compounds, Wöhler and Liebig observed that one atom of hydrogen in oil of bitter almonds C_7H_6O can easily be replaced by one of chlorine.

Not much attention was paid to these isolated facts before 1834, when Dumas found that chlorine can replace hydrogen in oil of turpentine atom for atom, and that this fact pointed to a natural law, for which he proposed the name of *Metalepsy* (*μεταληψις*, exchange).†

Other electro-negative elements can be found to act in a similar way, and from his own experiments, as well as those of others, he deduced his "*empirical law of substitution.*":—

(1) If in a body containing hydrogen this element is removed by means of chlorine, bromine, iodine, or oxygen, it takes up for each atom which it loses one atom of the three former, or half an atom of oxygen.‡

(2) If the compound contains oxygen the same rule holds good without any modification.

(3) But if the body contains water, first the hydrogen of the latter is removed without any replacement, and only then substitution takes place as stated under (1).

The third law he intended to account for the transformation of alcohol, which he regarded as a hydrate of ætherin C_2H_4, H_2O, into chloral C_2HCl_3O.||

He expressly pointed out that these laws were deduced from well established facts, and that such a deduction ought to precede the framing of a theory.

Among the younger French chemists working in the same direction as Dumas, the next step in advance was made by

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* Leçons de Chimie.

† Mem. Acad. Scienc. XV., 548.

‡ In explanation of this sentence, it must be remarked that hydrogen being the unit, the atomic weight of oxygen was by Berzelius and Dumas believed to be 16; Liebig, as well as most other German and English chemists, however, used the equivalent weight 8, and that of carbon was universally assumed to be 6. In order to avoid confusion, I have therefore transcribed the original formulæ of the different authors into those now in common use.

|| Ann. Chim. Phys. (2), LV., 140.

Laurent,* who found that there exist cases in which the number of equivalents of oxygen or chlorine entering a molecule is larger or smaller than that of the hydrogen removed, even in the case of bodies containing no oxygen, and consequently no water; thus, Dumas' third law did not hold good. At the same time Laurent lays stress on the fact, that in those cases where hydrogen is substituted by chlorine atom for atom, the products exhibit certain analogies with the original substance, and continues :—

"Many organic bodies when acted upon by chlorine lose a certain number of hydrogen-equivalents, which are given off in the form hydrochloric acid, and are replaced by an equal number of chlorine equivalents, and thus the physical and chemical properties of the original body do not undergo an essential change. Consequently the molecules of chlorine occupy the space left empty by the molecules of hydrogen, and the *chlorine plays in the new compound the same part as the hydrogen in the original body.*"

Dumas opposed such views, saying his law was merely empirical; and when Berzelius attacked him by mistake, instead of Laurent, pointing out that the new theory was in contradiction to the fundamental principles of the science, and that Dumas had overlooked the electro-chemical difference between hydrogen and chlorine, the latter replied : "Berzelius attributes to me an opinion precisely contrary to that which I have always maintained, namely that the chlorine takes *The Place* of the hydrogen. I have never said anything of the kind, neither can anything of the kind be deduced from the opinions I have put forward with regard to this order of facts. To represent me as saying that chlorine replaces hydrogen and fulfils the same functions, is to attribute to me an opinion against which I protest most strongly, as it is opposed to all that I have written upon these matters."†

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* Chemical Method, 199.

† I do not intend to refer in the sequel to all the memoirs and other publications on this subject. The following are the more important ones ;—Jour. Pharm., Mai, 1834; Dumas, Traité de Chim. V.; Ann. Chim. Phys. (2) LIX., 219, 319, 405, 487; LX., 223, 327; LXI., 125; LXVI., 326; LXXII., 407; LXXIII., 73; Compt. rend. I., 440; II., 130; VI., 633, 647; VIII., 609; X., 149, 409, 511. Further compare :—Ann. Chem. Pharm. XXXII., 101; XXXIII., 258. Laurent, Méthode de Chimie; Quesneville, Revue I., 5, 164, 399; II., 50. Sketches of the history of the theory of substitution are also found in Kekulé, Lehrbuch. Ladenburg, Entwicklungsgeschichte, &c. Wurtz, histoire des doctrines chimiques, and Kopp, Entwicklung der Chemie, &c.

Dumas would not be responsible for the gross exaggeration with which, in his opinion, Laurent had invested this theory. But when the latter had studied a larger number of substitution-products, when our knowledge of such bodies was largely increased by the researches of Regnault and Malaguti, and when Dumas himself had discovered trichloracetic acid and found that this body bore greater resemblance to the mother-substance than any other previously known substitution-product, then he accepted Laurent's theory and helped to work it further out.

Laurent however never acknowledged this, and in his *méthode de chimie* (published in 1854 only after his death) he endeavoured to prove that the pith of the theory was his creation, and that his propositions and those of Dumas had nothing in common but the word substitution.

In 1836 he published the principles of a theory of organic compounds, which afterwards was more fully worked out. Although never generally accepted, it must here be shortly mentioned, because Gmelin applied it in his hand-book to the division and classification of organic compounds.

According to it every organic compound contains a certain group of atoms called a *nucleus* (*noyau*). *Primary nuclei* consist of hydrocarbons, and their constitution may be compared with that of a prism, the atoms of carbon forming the solid angles and those of hydrogen the edges. The latter element may be replaced by equivalent quantities of chlorine or other elements without an essential change in the shape of the prism. Thus are obtained *secondary nuclei* or substitution-products having chemical properties resembling to a large extent those of the primary nucleus.

But if we remove from the prism an edge without replacing it by another, the whole falls to pieces; the compound undergoes decomposition.

Further, we may join to the prism elements or groups of atoms in the shape of pyramids, or completely surround it by such, and remove those again, without altering its original form.

The following table, containing the derivations of etherene (olefiant gas) may serve to illustrate his system.* It will be observed that his formulæ are double those which we now use, as Laurent held the view that all compounds contained an even number of atoms :—

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* Ann. chem. phys. LXIII., 377.

Ethérène	C_4H_8
Hydrochlorate	$C_4H_8 + H_2Cl_2$
Chloréthérase	$C_4H_6Cl_2$
Hydrochlorate	$C_4H_6Cl_2 + H_2Cl_2$
Chloréthérese	$C_4H_4Cl_4$
Hydrochlorate	$C_4H_4Cl_4 + H_2Cl_2$
Chloréthérise	$C_4H_2Cl_6$
Hydrochlorate	$C_4H_2Cl_6 + H_2Cl_2$
Chloréthérose	C_4Cl_8
Chloride éthérosique	$C_4Cl_8 + Cl_4$
Chloral	$C_4Cl_6O + H_2O$
Bromal	$C_4Br_6O + H_2O$
Iodal	$C_4I_6O + H_2O$.

The principle of the nomenclature, first proposed by Dumas and Peligot, is easily understood.

These formulæ, although probably suggested by considerations based on the theory of radicals, bear more resemblance to those used in the theory of ætherin; they also differ from the former, which had supposed compound radicals to contain an uneven number of atoms.

CHAPTER III.

Dumas' Theory of Types.—Berzrlius' Conjugated Formulæ.—Liebig's Attacks on the French Chemists.—Inverse Substitution.—Development of the Radical Theory.—Liebig's Theory of Polybasic Acids.—Gerhardt and Laurent.—Unitary Formulæ.

From the theory of substitution Dumas* derived his theory of chemical types. He published an outline of it in which he stated the following propositions:

(1) The elements of a compound body can, in many cases, be replaced by equal equivalents of other elements or of compound bodies, which play the part of simple substances.

(2) When such a substitution, equivalent for equivalent, occurs, the body in which such a displacement has taken place retains its *chemical type*, and the element which has entered *plays in it the same part* as that which had been removed.

Besides chemical types, he also assumed, following Regnault, the existence of *molecular* or *mechanical* types.

To the same chemical type all bodies belong which derive from each other by simple substitution, such as acetic acid

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* Ann. Chim. Phys. LVIII., 305.

$C_2H_4O_2$ and trichloracetic acid $C_2HCl_3O_2$; aldehyde C_2H_4O and chloral C_2HCl_3O; chloroform $CHCl_3$, bromoform $CHBr_3$, and iodoform CHI_3. Compounds belonging to the same mechanical type contain also the same number of equivalents, but possess essentially different properties, as alcohol and acetic acid, whose formulæ were then $C_4H_6O_2$ and $C_4H_4O_4$ ($C = 6$; $O = 8$).

He then points out that the properties of a compound depend chiefly on the arrangement and not on the nature of its atoms. In opposition to the binary theory of Berzelius he proposed a unitary one, and compared chemical compounds to a planetary system, the different atoms being kept together by their mutual attraction. If one atom of a body be replaced by one of another, the system remains intact, even on substituting an element by a compound one (compound radical), the chemical constitution not undergoing any change.

Naturally Berzelius could not accept such views. When Laurent in 1835 published his researches on the action of chlorine upon naphthalene, Berzelius tried to show that the different chlorinated compounds which Laurent obtained must be regarded as chlorides of different hydrocarbon-radicals, and to Laurent's later views he paid so little attention that in his anniversary report for 1836 he only says it was quite superfluous to dwell on a theory of such a kind.

But when Dumas brought out his views and sent a challenge to Berzelius, the battle soon commenced. Dumas said: "These electro-chemical conceptions, this special polarity which has been assigned to the elementary atoms, do they really rest on such evident facts that they might be accepted as articles of faith? Or, if we regard them only as hypotheses, do they possess the property of adapting themselves to facts; are they capable of explaining them; can we assume them with such a complete certainty that in chemical investigations they appear as useful guides? We must admit that such is not the case."

Berzelius and his adherents now commenced an exasperated fight against Dumas and his followers, from which the views of the adherents of the theory of substitution and types in a modified and improved form, but correct in the fundamental principles, came out as victors. While one side had to recur to legions of new, and always more complicated, hypotheses, the other brought into the field a most effective weapon, a continually growing army of new discoveries.*

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* Kekulé, Lehrb. I., 69.

Berzelius saw clearly that it was impossible to bring his views into accordance with those of Dumas, and that if he was to succumb, the chemical theory which he had constructed with such diligence and zeal would tumble to pieces.*

As one of the best proofs of the correctness of his views, Dumas showed that acetic acid and trichloracetic acid are strictly analogous compounds; that, by the replacement of three atoms of hydrogen by chlorine, the saturating capacity of acetic acid remains the same in the new compound, and when Berzelius ironically asked, what other proofs he had to bring forward, he showed that by the action of alkalis they undergo analogous decomposition: acetic acid being resolved into carbonic acid and marsh gas, and trichloracetic acid into carbonic acid and chloroform or trichlorinated marsh gas, which decompositions are expressed by the equations ($C = 6$; $O = 8$):

$$C_4H_4O_4 = C_2O_4 + C_2H_4$$
$$C_4HCl_3O_4 = C_2O_4 + C_2HCl_3.$$

Berzelius however could not agree to that; he pointed out the dissimilarities of the two bodies, and endeavoured to prove that their fundamental properties were quite different. Acetic acid contained the radical acetyl C_4H_3, while trichloracetic acid consisted of oxalic acid combined with a chloride of carbon:—

Acetic acid .... $C_4H_3,O_3 + HO$
Trichloracetic acid .... $C_2Cl_3 + C_2O_3 + HO.$

This view he extended to the consideration of other substitution-products, and in order to do so he found himself obliged to double or triple the simple formulæ of different compounds, which thus became often very complicated. Thus he resolved dichloroformic ether $C_6H_6Cl_2O_4$ into $2C_2HO_3 + C_2HCl_3 + 2C_4H_3O_3 + C_4H_3Cl_3$, or regarded it as a compound conjugated of anhydrous formic acid, formyl chloride, anhydrous acetic acid, and acetyl chloride; and dichlorether $C_4H_3Cl_2O$ (tetrachlorethyl oxide), in the same manner as anhydrous acetic acid copulated to acetyl chloride $C_4H_3O_3 + 2C_4H_3Cl_3$.

Such and similar formulæ could not of course find universal assent. Liebig opposed them, saying that the views of Berzelius rested on a number of hypothetical assumptions, for which any kind of proof is wanting, and he remarks most appropriately that even in inorganic chemistry the metal contained in permanganic acid could be replaced by chlorine without producing a change of form, and yet there could not exist a greater dissimilarity than that between chlorine and manganese. Such facts must be taken for what they are; if chlorine can replace manganese without altering the nature of the compound, why should not chlorine and hydrogen exhibit a similar behaviour?*

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* Kekulé I., 72.

Again, he says that Berzelius was the first who regarded organic acids, ether, &c., as oxides of compound radicals, and this view was a guiding star in a labyrinth in which nobody could find his way. But the analogies between inorganic and organic compounds, which Berzelius had first made out, were not general; up to a certain point we might, in the investigation of organic bodies, follow the principles of inorganic chemistry, but not beyond, where they created complications instead of solving them; here new principles were required.†

On the other hand he attacked the French chemists; the nucleus theory of Laurent appeared to him to be unscientific, useless, and pernicious.‡ To some extent he was justified in making such remarks. Laurent was a highly intellectual and gifted man, but he did not hesitate to propound hypotheses for which no proofs could be obtained, although such were afterwards found in many cases.

Liebig opposed Dumas as going too far, inasmuch as the latter assumed that the carbon in organic compounds could be replaced by substitution.|| In order to combat this view he used the weapon of satire, which he could handle most skilfully.

In the "Annalen,"§ edited by him, appeared, 1840, a letter dated from Paris, signed S. C. H. Windler (*anglicè*, S. Windler), in which the writer informs the chemical public that he had succeeded in replacing in acetate of manganese not only the hydrogen by chlorine but also the metal, the oxygen, and finally the carbon; yet the new substance, although consisting entirely of chlorine, still possessed the principal properties of the original compound. He continues:

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* Ann. Pharm. XXXI., 119.

† Ann. Pharm. XXXII., 72.

‡ Ibid. XXIV., 1.

|| The fact on which Dumas founded this hypothesis is a very singular one, and even to-day very few analogous reactions are known. Walter found that by the action of sulphuric acid on camphoric acid $C_{10}H_8O_4$, the latter was converted into sulphocamphoric acid $C_9(SO_2)H_8O_4$, from which Dumas concluded that the group SO_2 could replace an atom of carbon.

§ Ann. Chem. Pharm. XXXIII., 305.

"*Quoique je sache, que dans l'action décolorante du chlore il y a remplacement de l'hydrogène par le chlore et que les étoffes, qu'on blanchit maintenant en Angleterre d'après les lois de substitutions conservent leur types, je crois néanmoins que la substitution du carbone par le chlore atome pour atome, est une découverte qui m'appartient.*"

A foot note is added :—

"*Je viens d'apprendre qu'il y a déjà dans les magasins à Londres des étoffes en chlore filé, très recherchées dans les hopitaux et préférées à toutes autres pour bonnets de nuit, caleçons, etc.*"

Facts, however, rapidly increased, proving the correctness of the substitution theory, as far as the replacement of hydrogen is concerned, and it was found the products resembled the original substance in their principal properties. Of still more importance was the discovery that such products could by *inverse substitution* be reconverted into the original compound. Melsens found (1842) that by the action of potassium-amalgam on an aqueous solution of trichloracetic acid the latter was again transformed into acetic acid.

This and similar facts did, however, not shake Berzelius' faith. He came now to the conclusion that acetic acid was a compound of methyl and oxalic acid $C_2H_3 + C_2O_3 + HO$. In a similar way he wrote the formulæ of other compounds, which yield substitution products. They all contain a group consisting of carbon and hydrogen, a *copula**, and, according to him, in this only substitution can take place. He was so convinced of the correctness of this view, that he could not understand how anybody could hold another opinion.

When Hofmann,† in 1845, discovered the chlorinated anilines, bases in which hydrogen is replaced by chlorine, Liebig in a note to this important paper, more distinctly than he had done before, assented to the new views, saying that he believed the nature of a compound did not depend on the nature of its elements, but the position which they occupy. To this Berzelius replied, that all organic bases were copulated or conjugated ammonias; thus aniline was $C_{12}H_4, NH_3$ and chloraniline $C_{12}H_3Cl, NH_3$; both contained ammonia as the basic constituent; the composition of the copula was of no consequence.

From this time, however, Berzelius' opposition against the theory of substitution began to grow lame, while his followers, in their joy over the discovery of the copula, completely forgot that his opposition originally had for its object to combat the theory of substitution. Laurent's opinion that on substitution, chlorine replaced hydrogen and undertook its functions, was now acknowledged by them. What formerly had appeared absurd became now, in the light of the copula theory, at once clear and simple.

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* This term was first used by Gerhardt, and adopted by Berzelius, who, however, employed it in a different sense, as will be shown further on.

† Ann. Chem. Pharm. LIII., 12.

Berzelius remained true to the electro-chemical theory to the end of his life, and when he developed this theory in his handbook, 1827, he said prophetically:

"The habit of an opinion often leads to the complete conviction of its truth; it hides the weaker parts and makes us incapable to accept the proofs against it."

His formulæ became more and more complicated, because he was forced to introduce no end of utterly hypothetical radicals, and, after his death in 1848, his followers had the greatest trouble to reconstruct anew radicals out of his copulæ.

Meanwhile the radical theory had obtained important support by Bunsen's classical researches on cacodyl and its compounds, which contain in common the groups C_2H_6As, possessing the characters of a metal, and which can be obtained in the *free state.**

After this Kolbe and Frankland succeeded in obtaining hydrocarbons which, with regard to their mode of formation and empirical formulæ, were considered to be the radicals contained in the alcohols. The isolation of the so-called alcohol radicals was naturally hailed with great joy by the adherents of the radical theory, and later investigations of them have given great help to the devolopment of organic chemistry.

The old question whether a radical could contain oxygen was still discussed; Berzelius of course had opposed such an opinion most strenuously; thus he says, in 1843, it was as inadmissible as the assumption that sulphurous acid was the radical of sulphuric acid, or manganese peroxide that of permanganic acid. "*An oxide cannot be a radical. The idea of the word radical includes that it means a body which in an oxide is combined with oxygen.*"

The introduction of the substitution theory into the radical theory led to the conception of substituted radicals. The adherents of the electro-chemical theory had to make the concession that electro-negative chlorine could occupy the place of electro-positive hydrogen without materially altering the chemical properties of the compound. But if chlorine would do this, why not also oxygen? The radical theory was never in want of hypotheses, and thus some went as far as to assume that when chlorine replaces hydrogen, or *vice versa*, these elements, or at least one of them, possessed in such a case electro-chemical properties different from those which they generally exhibit.

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* Ann. Chem. Pharm. XLII., 14.

The further development of the theory of substitution and of the types led to a more precise definition of a product of substitution and to clearer conceptions of the terms: *equivalent*, *atom*, and *molecule*. This was in the first line effected by the development of the theory of polybasic acids. According to the dualistic theory the neutral (normal) oxysalts were regarded as compounds of a basic oxide with an acid (acid forming oxide), and acid salts as compounds of a normal salt with the hydrate of an acid. Thus sulphuric acid and its potassium salts were written in equivalent formulæ:

Sulphuric acid (first hydrate) ...$HO.SO_3$
Neutral sulphate of potash ......$KO.SO_3$
Acid sulphate of potash ....$KO.SO_3 + HO.SO_3$.

The quantity of an acid salt as represented by its formula contained therefore twice as much acid as the neutral salt. But an exception was made in the case of phosphoric acid, citric acid, and their salts, because their formula could not be divided without obtaining fractions of atoms:

$$\begin{array}{ccc} & \multicolumn{2}{c}{\text{Acid Salts.}} \\ PO_5.3HO & \overbrace{PO_5 2HO.NaO \qquad\qquad PO_5.HO.2NaO} & \\ C_{12}H_5O_{11}.3HO, & C_{12}H_5O_{11}.2HO.NaO, \quad C_{12}H_5O_{11}.HO.2NaO, & \end{array}$$

Normal Salts.

$$PO_5.3NaO$$
$$C_{12}H_5O_{11}.3NaO.$$

These acids were called tribasic because their formulæ cannot be divided by three; and if an acid formed acid salts besides normal ones, Berzelius considered it as polybasic only if the formulæ of these compounds were indivisible.

After Graham had more exactly studied the different modications of phosphoric acid, and Liebig had examined a great number of organic acids and their salts, the latter published his theory of polybasic acids.* He showed that a number of acids exist which, analogous to phosphoric acid, can take up 1 and 2 or 1, 2 and 3 equivalents of a base. Such he regarded as polybasic acids even if their formulæ could be divided; and, as the most characteristic property of a polybasic acid, appeared to him that it could form double salts or take up different bases at the same time.

In the same memoir he also discussed the question whether the oxyacids or their salts are compounds of water or a basic oxide with an acid oxide, or whether the older views of Davy and Dulong were more correct, according to which all acids and salts may be represented as combinations of hydrogen or a metal with an element or a group of elements. This latter view would do away with Berzelius' classification of these compounds as hydracids and oxyacids, haloïd salts and amphid salts, but in Liebig's opinion such a view, according to which the acids would simply appear as salts of hydrogen, was more applicable to organic than to inorganic compounds, and the older views prevailed for a long time until they were gradually given up.

The theory of polybasic acids was further developed by Gerhardt and Laurent, whose names will always remain inseparable in the history of our science. With immutable perseverance they endeavoured to remove those older views on the constitution of chemical compounds which they recognised as incorrect. By their ingenious speculations on the relative weights of atoms and molecules, these terms were first precisely defined, and almost all the arguments they used hold good up to the present day, and thus they have taken a foremost place in the erection of the present chemical system. They contributed to this much by developing Liebig's views, and by carrying them consistently through.

According to Gerhardt, an acid must be regarded as polybasic if it forms acid and double salts with any bases, or if it contains more than one atom of hydrogen which can be replaced by metals; but the most characteristic criterion of such an acid he finds in the fact that it can form several compound ethers, viz.: that the different atoms of hydrogen which may be exchanged for metals can also be replaced one after the other by alcohol radicals.

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* Ann. Pharm. XXVI., 113.

Laurent accepted these views, and added as another characteristic that a monobasic acid could form only one amide, a dibasic two, of such compounds, &c.

They wrote the formula of all salts and ethers, both acid and normal, in expressions of the same type as that of the acid itself; thus sulphuric acid and its derivatives were written, using the old equivalent weights, as follows:—

Sulphuric acid	$H_2S_2O_8$.
Neutral potassium salt	$K_2S_2O_8$.
Acid potassium salt	KHS_2O_8.
Neutral ether	$(C_4H_5)_2S_2O_8$.
Ethylsulphuric acid	$(C_4H_5)HS_2O_8$.

We find here one of the first attempts to ascertain the relative weight of different molecules by the study of chemical analogies. This method was generally followed by Laurent, who always endeavoured to interpret similar chemical reactions in a conformable manner. He showed thus that a molecule of chlorine must consist of two atoms, because when this element acts on organic bodies 2, 4, 6, &c., atoms enter into action, and never 1, 3, 5, &c.

To the same conclusion he was led by a comparison of the action of chlorine with the matamorphoses which cyanogen chloride, benzoyl chloride, and other acid chlorides undergo under certain conditions. He clearly proved that if a molecule of cyanogen chloride can be divided into *two parts,* the same arguments apply with equal force to chlorine itself.

Gerhardt founded his speculations chiefly on Avogadro's hypothesis, according to which equal volumes of different gases at the same temperature and pressure contain the same number of molecules. The relative weights of the molecules could therefore be easily determined, and the true atomic weights be ascertained, by defining the latter term as the smallest quantity of an element existing in a molecule of one of its compounds.

The merits of the two men were hardly recognised during their lifetime, and only Gerhardt lived just long enough to have the satisfaction of seeing his views generally accepted.

When in 1843 he first proposed to double the old atomic weights of oxygen, sulphur, and carbon, he encountered a violent opposition. Berzelius found his proposal so absurd that he deemed it unnecessary to mention it in his annual report.

In order to give a sound foundation to their theoretical views, Laurent and Gerhardt made numerous original researches; but the results of their work, even when correct, were received coldly and not without doubts, while any mistakes of theirs were judged very harshly. It is true that the great talent which both possessed to arrange a number of facts under a common point of view led them often astray, and that some of their assertions rested on the slippery ground of theoretical speculation instead of the sound foundation of experimental research. Anyhow their views were generally held to be unscientific and confused. Liebig attacked them vigorously, but being treated without consideration, and while they were convinced of the truth of their theories, their retorts were as inconsiderate as the attacks.* The chemists of the old school were offended by the provoking tone in which Laurent and Gerhardt condemned their views and by the assurance with which they brought forward their own, and in consequence the two great chemists had to suffer a treatment which it is now quite painful to think of.†

In order to keep chemistry free from all fictions they at first used only empirical formulæ, expressing simply the composition of the molecule, because according to Laurent the adherents of the radical theory had succeeded in converting chemistry into the science of non-existing bodies. Liebig's satire against the theory of substitution Laurent turned against him by announcing the discovery of a group of atoms which he named *Eurhyzene*, and which, although having all the characteristics of a compound radical, was nothing but hydrogen peroxide.

If we look back to such discussions they now appear to us strange enough. Berzelius tried to ridicule the notion of radicals containing oxygen by saying in such a case sulphurous acid (sulphur dioxide) might be regarded as the radical of sulphuric acid. Now this is the very view held to-day; this acid may be regarded as a combination of sulphur dioxide (sulphuryl) with two half-molecules of hydrogen peroxide (hydroxyl), both groups fulfilling the conditions which Liebig required to constitute compound radicals.

The use of empirical formulæ, or unitary as they were also called in contrast with the binary or dualistic of the radical theory, had some great advantages. Any compound, whether consisting only of two or of more elements, appeared as a chemical whole and not as composed of different proximate components of which each formed a closed group of atoms.

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* See Ann. Chem. Pharm. LVII., 93, 388; LVIII., 227.

† Kopp, Entw. Chemie, 628.

The common bond by which analogous compounds are connected could be more clearly perceived and the facts directly compared with each other, instead of looking at them through the deceptive glass of inherited hypotheses.* Certain groups of compounds could be brought under a common point of view and their composition be expressed by general formulæ such as $C_mH_nO_c$, and by means of these the chemical changes of such a group be expressed by general schematic equations. Laurent and Gerhardt were therefore ridiculed and taxed with the reproach that they practised chemical algebra. The exclusive use of unitary formulæ showed, however, soon that in many cases they do not represent the relations of bodies in such a clear manner as those of the radical theory. But Gerhardt and Laurent objected to the latter, because they held the view that it was not possible to ascertain the proximate constituents of compounds from a limited number of decompositions or combinations.

In order to render conspicuous certain relations, they used therefore so-called synoptical formulæ, in which such groups of atoms as remain together in a series of chemical changes were written separately from the rest or expressed by a certain symbol. These formulæ bore more or less resemblance, sometimes to the theory of radicals, and sometimes to that of the nucleus theory, just as it was found most convenient; they were not intended to express the constitution of a body.

CHAPTER IV.

INTRODUCTION OF RADICALS INTO THE TYPES.—THEORY OF RESIDUES.—DISCOVERY OF THE COMPOUND AMMONIAS BY WURTZ AND HOFMANN.—WILLIAMSON'S WATER TYPE.—GERHARDT'S THEORY OF TYPES.—CONDENSED TYPES.—CONJUGATED COMPOUNDS.—THE BEGINNING OF THE THEORY OF VALENCY.

The greatest progress which organic chemistry next made was the introduction of the radicals into the types, leading to an amalgamation of both theories, which of course was brought about very gradually.

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* Kekulé, Lehrb., I., 84.

Already Dumas, when expounding his theories of substitution and types, had called attention to the fact that not only elements, like chlorine, but also groups of atoms such as NO_2 can replace hydrogen in a compound, and that these, which occur in certain types, may again be exchanged for simple bodies; such groups therefore deserved the name of compound radicals.

Gerhardt adopted this idea in 1839, but did not admit, with the adherents of the radical theory, that such a group formed a chemical whole. This latter view had however already been opposed by Liebig[*] in 1835, who hoped that the time would not be distant when in organic chemistry the idea of unchangeable radicals would be given up, and who in the next year pronounced the opinion that in the formation of an organic acid, that of the radical contained in it need not in any way precede it.[†]

In discussing a question which was not settled in 1839, *i.e.*, whether ether was an oxide of ethyl or a compound of olefiant gas and water, Liebig[‡] showed that the analogy of the compounds of ammonia with those of ethyl, which Dumas and Boullay had pointed out, might also be illustrated by assuming that the former contained the radical amidogen NH_2, and the latter acetyl C_4H_3, or the radical of acetic acid. From such a point of view both hypotheses of the constitution of ether appeared equally well founded, and any further discussion became superfluous.

In the same year Gerhardt published his views in regard to the process taking place, when a simple body is replaced by a compound. This he did not consider as a substitution of an element by a compound radical, but as a combination of two residues into a unitary whole, as opposed to an articulated binary compound. Such groups of atoms which generally were called compound radicals, he first called "*le reste*" or "*le restant*," and afterwards he worked out his "*théorie des residus*," according to which such a rest or residue might have the composition of a compound radical, but while the latter was believed to exist in the compound as a definite closed group of atoms, this was not the case with a residue. Thus by the action of nitric acid on ethyl alcohol we obtain ethyl nitrate:

$$C_2H_6O + HNO_3 = C_2H_5NO_3 + H_2O.$$

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[*] Ann. Pharm. XIV., 166.

[†] Ann. Pharm. XVIII., 223.

[‡] Ibid. XXX., 138.

The radical theory assumed ethyl alcohol to be the hydrate of oxide of ethyl (or a hydroxide, as we call it now), and consequently regarded ethyl nitrate as a compound of ethyl oxide with anhydrous nitric acid (nitrogen pentoxide), and wrote its formula, using the equivalent weights, C_4H_5O,NO_5. But according to Gerhardt's opinion in the above reaction nitric acid loses one atom of hydrogen, and ethyl alcohol the group OH, and the residues thus formed combine to the unitary compounds: water and ethyl nitrate.

These views found more and more acceptance; the theory of radicals was supplanted by that of residues, and thus our present conception of a compound radical was brought about, which, introduced into the theory of types, led to the fusion of the two theories.

The first step in this direction was the discovery of the compound ammonias by Wurtz in 1845. The existence of such bodies had been predicted by Liebig, who stated that by combining an alcohol radical with amidogen NH_2 a body would be obtained possessing the character of common ammonia.*

Wurtz followed up this view; thus ethylamine, or ethyliaque, as he called it, was formed by the union of the two radicals or residues C_2H_5 and NH_2.

This body might also be looked upon, in accordance with Berzelius' views, as a conjugated ammonia containing olefiant gas as copula, a view calling back the ætherin theory. In his classical researches on aniline Hofmann inclined first to this view. But soon he met with facts proving that the compound ammonias or amines are substitution products, being formed by replacing, in ammonia, hydrogen by an alcohol radical. In fact he succeeded in replacing not only one, but also the second and the third atom of hydrogen in ammonia by such radicals, and thus obtaining compounds still possessing the character of ammonia.

By this introduction of radicals or residues in the theory of types, the latter soon extended its boundaries. The discovery of bases possessing a constitution analogous to that of ammonia is, without a doubt, the foundation-stone of our present theoretical views. Organic compounds were now referred to, or compared with, the simplest inorganic compounds as their *type*;

*Handwörterbuch, I., 698.

in the type *ammonia* hydrogen could not only be replaced atom for atom by metals (Laurent), but also by alcohol radicals.*

Williamson demonstrated in 1850, that in an analogous manner the alcohols and their ethers can be referred to the type *water*; by replacing in water half its hydrogen by an alcohol radical, we have an alcohol which, by substituting the same or a similar radical for the second hydrogen atom, is converted into an ether.†

Williamson further pointed out that acetic acid might be considered as water, in which one atom of hydrogen is replaced by the radical C_2H_3O, which, to distinguish it from Berzelius' acetyl C_2H_3 he called *othyl* (oxethyl). At the same time he predicted a class of bodies which would be formed by replacing the second hydrogen atom by the same or a similar acid radical, and which therefore would bear the same relation to the acids as the ethers to the alcohols.‡

Gerhardt discovered these compounds, which he called *anhydrides*, in 1852; now he and others endeavoured to find among the more simple inorganic bodies types for organic compounds. Thus Gerhardt's theory of types arose, according to which organic bodies may be classed under the four types of *hydrogen*, *hydrochloric acid*, *water*, and *ammonia*, as the following table will illustrate:—

Hydrogen .... $\left.\begin{matrix}H\\H\end{matrix}\right\}$	Hydrochloric Acid .... $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$	Water ...... $\left.\begin{matrix}H\\H\end{matrix}\right\}O$	Ammonia.... $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$
Ethyl Hydride ... $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}$	Ethyl Chloride.. $\left.\begin{matrix}C_2H_5\\Cl\end{matrix}\right\}$	Ethyl Alcohol $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	Ethylamine.. $\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N$
Ethyl ..... $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}$	Benzoyl Chloride $\left.\begin{matrix}C_7H_5O\\Cl\end{matrix}\right\}$	Ethyl Ether ..$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$	Diethylamine $\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N$
Acetyl Hydride....(Aldehyde) $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}$	Acetyl Chloride $\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\}$	Acetic Acid .. $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$	Triethylamine $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N$
Acetylmethyl..(Acetone) $\left.\begin{matrix}C_2H_3O\\CH_3\end{matrix}\right\}$	Cyanogen Chloride.... $\left.\begin{matrix}CN\\Cl\end{matrix}\right\}$	Acetic Anhydride..$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O$	Acetamide.... $\left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N$

To the first type therefore belong the hydrocarbons, the aldehydes and acetones, and to the second, besides the chlorides, the bromides and iodides; the third type included not only the alcohols, ethers, monobasic acids, and anhydrides, but also such sulphur compounds as might be regarded as derived from the former by replacing the *extra radical* oxygen by sulphur, while compounds of phosphorus and arsenic, having a constitution analogous to the amines, were placed into the ammonia type.

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* Kekulé, Lehrb. I., 91.

† Brit. Ass. Rep., 1850-55.

‡ Journ. Chem. Soc., IV., 237.

The next step forward was the introduction of condensed types. In the paper already referred to, Williamson showed that the bibasic sulphuric acid might be regarded as being derived from two molecules of water, the radical of the acid replacing at the same time one atom of hydrogen in each molecule. He extended this view to other bibasic acids, which he classed under the double water type, just as the monobasic acids are derived from a single molecule of water.

Type.	Acetic Acid.	Nitric Acid.
$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$	$\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O$
Type.	**Succinic Acid.**	**Sulphuric Acid.**
$\begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}O\\\left.\begin{matrix}H\\H\end{matrix}\right\}O\end{matrix}$	$\left.\begin{matrix}H\\C_4H_4O_2\\H\end{matrix}\right\}\begin{matrix}O\\O\end{matrix}$	$\left.\begin{matrix}H\\SO_2\\H\end{matrix}\right\}\begin{matrix}O\\O\end{matrix}$

In 1854 Williamson showed that by heating chloroform $CHCl_3$ with sodium ethylate, a compound which he called tribasic formic ether $CH(OC_2H_5)_3$ is obtained, and that this as well as chloroform might be regarded as belonging to triply condensed types:—

Type.	Formyl Trichloride (Chloroform).	Type.	Tribasic Formic Ether.
H_3Cl_3	$CHCl_3$	$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}CH\\(C_2H_5)_3\end{matrix}\right\}O_3$

Odling* extended these views; he applied them to a large number of compounds, and Gerhardt† adopted the theory of condensed types in 1856. It soon found a powerful support in Berthelot's researches on glycerine and its derivatives, first correctly interpreted by Wurtz, who, by his brilliant discoveries of the glycols and other compounds, as well as by his ingenious speculations, became one of the chief promoters of the theory of types.

As a replacement of more than one atom of hydrogen by a radical had been first observed in the case of polybasic acids, such radicals were at first called *polybasic*, which afterwards was changed into *polyatomic*, *polygenic*, or *polyvalent*.

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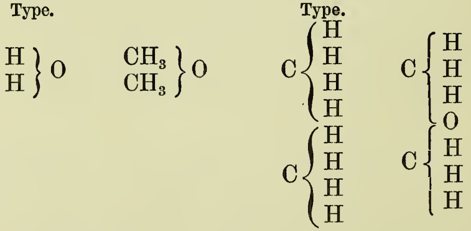
* Quart. Journ. Chem. Soc. VII., 1.

† Traité Chem. Org. IV., 581.

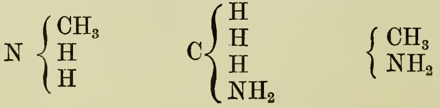
It has already been mentioned that, according to Gerhardt's views, radicals did not exist in a compound as proximate constituents. A radical is, according to him, nothing but a mere residue of a molecule, or a group of atoms which remain together in a number of chemical changes. Such changes consist mostly of double decompositions or reciprocal reactions; in the more simple ones elements exchange their places; but a simple body may replace, or be replaced by, a group of atoms, which we then call a compound radical. It is a matter of indifference whether such a group can be isolated or not.

The typical formulæ did not pretend to explain the position of the atoms in the molecules; they only intended to express in a convenient manner a certain number of changes which the compound may undergo, or by which it has been formed. Consequently one and the same body may be referred to different types. Thus methyl ether C_2H_6O, which according to Gerhardt belonged to the water type, could also, after Kekulé had added the new type of marsh gas CH_4, be considered as a derivative of the latter, *i.e.*, as consisting of two residues of marsh gas which are held together by oxygen :



$$\overset{\text{Type.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} \qquad \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}O \qquad \overset{\text{Type.}}{\begin{matrix}C\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right.\\C\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right.\end{matrix}} \qquad \begin{matrix}C\left\{\begin{matrix}H\\H\\H\end{matrix}\right.\\O\\C\left\{\begin{matrix}H\\H\\H\end{matrix}\right.\end{matrix}$$

If we replace one atom of hydrogen in ammonia by methyl we obtain methylamine CH_5N ; this compound is therefore a substituted ammonia ; but it may also be looked upon as marsh gas, in which one atom of hydrogen has been replaced by amidogen NH_2, or, as it is formed by the union of the two residues CH_3 and NH_2, we can also refer it to the hydrogen type :



$$N\left\{\begin{matrix}CH_3\\H\\H\end{matrix}\right. \qquad C\left\{\begin{matrix}H\\H\\H\\NH_2\end{matrix}\right. \qquad \left\{\begin{matrix}CH_3\\NH_2\end{matrix}\right.$$

The first member of the glycols or alcohols of bivalent radicals which Wurtz discovered was ethene alcohol $C_2H_6O_2$; it is obtained by combining olefiant gas with bromine and replacing in the ethene dibromide thus obtained, the halogen by hydroxyl. These compounds may therefore be expressed by the following formulæ:—

$$\text{Ethene dibromide}\ldots\left.\begin{array}{r}C_2H_4\\Br_2\end{array}\right\}\qquad C_2H_4\left\{\begin{array}{l}Br\\Br\end{array}\right.$$

$$\text{Ethene alcohol}\ldots\ldots\left.\begin{array}{r}C_2H_4\\H_2\end{array}\right\}O_2\qquad C_2H_4\left\{\begin{array}{l}OH\\OH\end{array}\right.$$

By the action of hydrochloric acid on the latter compound, one hydroyl is replaced by chlorine, and ethene chlorhydrate is formed, which on oxidation yields chloracetic acid, just as oxidising agents convert ethyl alcohol into acetic acid. Consequently the chlorhydrate can be regarded as monochlorethyl alcohol, but it may also be referred to the mixed type "hydrochloric acid-water," bivalent ethene replacing in each molecule of the two latter one atom of hydrogen; and finally it may be looked upon as a combination of chlorine hydroxyl and ethene,

$$\left.\begin{array}{r}C_2H_4Cl\\H\end{array}\right\}O\qquad C_2H_4\left\{\begin{array}{l}Cl\\OH\end{array}\right.\qquad \left.\begin{array}{r}\left.\begin{array}{r}Cl\\C_2H_4\end{array}\right\}\\H\end{array}\right\}O$$

By the action of ammonia on monochloracetic acid, we obtain amidacetic acid $C_2H_3(NH_2)O_2$. This compound is a monobasic acid, but at the same time it possesses some of the characteristic properties of a compound ammonia, just as chloracetic acid in some of its reactions resembles the chlorides of the alcohol radicals. The chemical relations of these compounds may therefore be expressed by the following formulæ:—

$$C_2H_2O\left\{\begin{array}{l}Cl\\OH,\end{array}\right.\quad \left.\begin{array}{r}C_2H_2ClO\\H\end{array}\right\}O,\quad \left.\begin{array}{r}C_2H_3O_2\\Cl\end{array}\right\},\quad \left.\begin{array}{r}\left.\begin{array}{r}Cl\\C_2H_2O\end{array}\right\}\\H\end{array}\right\}O$$

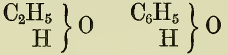
$$C_2H_2O\left\{\begin{array}{l}NH_2\\OH,\end{array}\right.\quad \left.\begin{array}{r}C_2H_2(NH_2)O\\H\end{array}\right\}O,\quad \left.\begin{array}{r}C_2H_3O_2\\NH_2\end{array}\right\},\quad \left.\begin{array}{r}\left.\begin{array}{r}\left.\begin{array}{r}H\\H\end{array}\right\}N\\C_2H_2O\end{array}\right\}\\H\end{array}\right\}O,\quad \left.\begin{array}{r}C_2H_3O_2\\H\\H\end{array}\right\}N$$

The two first formulæ express that both compounds contain the bivalent radical C_2H_2O; the two following tell us that they are substitution-products of acetic acid, and may, like the latter, be regarded as compounds of monad radicals, amidacetic acid being formed by replacing in chloracetic acid the chlorine by amidogen NH_2; chloracetic acid can also be referred to the mixed type $HCl - H_2O$, just as amidacetic acid to the type $NH_3 - H_2O$; and finally, the latter acid may also be regarded as a compound ammonia.

Such formulæ are still in use; which of them we prefer depends on the chemical relations or analogies which we wish to express; among them the one which represents the most important relations in the most simple manner being most generally used.

Already, 1838, Gerhardt's attention was called to the fact that by the action of sulphuric acid on different organic compounds, peculiar bodies are formed which do not exhibit the characteristic properties of the components, for instance, those now called sulphonic acids. In order to distinguish this kind of combination he termed it "*accouplement*," and the product "*sel copulé.*"

An example will suffice to show what he meant; ethyl alcohol C_2H_4O and phenyl alcohol (phenol) C_6H_6O were found to be compounds having many properties in common, both belonging to the type "water," their formulæ were written thus:



$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}C_6H_5\\H\end{matrix}\right\}O$$

On dissolving them in strong sulphuric acid, both are acted upon in apparently the same manner:

$$C_2H_6O + H_2SO_4 = H_2O + C_2H_6SO_4.$$
$$C_6H_6O + H_2SO_4 = H_2O + C_6H_6SO_4.$$

The two acids thus formed were then called ethylsulphuric and phenylsulphuric acids; they are both monobasic, but all their other properties are as different as possible. The ethyl compound is a very unstable body; on boiling it with water the inverse reaction by which it is formed takes place, sulphuric acid and alcohol being reproduced; while the second compound, which is now called phenolsulphonic acid, behaves quite differently—the presence of a residue of sulphuric acid in it can be only detected by completely destroying it.

Gerhalt developed his original views and modified them in different directions. Berzelius, who in his anniversary report commented upon them satirically, accepted in the next year the term copula, and, as already mentioned, made large use of it in his attacks on the theory of substitution.

The introduction of radicals or residues in the theory of types and the theory of conjugated compounds led to the notion of conjugated radicals, or groups containing several more simple groups as proximate constituents. Thus the following monobasic acids, belonging to the type of water, undergo under certain conditions an analogous decomposition, the residue carbonyl CO being taken out; formic acid yielding hydrogen at the same time, and the others an alcohol radical. The radicals contained in them were therefore regarded as being copulated of carbonyl and hydrogen, or alcohol radicals, and their original formulæ resolved as follows:

$$\begin{array}{ccc}
\text{Formic Acid.} & \text{Acetic Acid.} & \text{Propionic Acid.} \\
\left.\begin{array}{r}CHO\\H\end{array}\right\}O & \left.\begin{array}{r}C_2H_3O\\H\end{array}\right\}O & \left.\begin{array}{r}C_3H_5O\\H\end{array}\right\}O \\
\left.\begin{array}{r}H.CO\\H\end{array}\right\}O & \left.\begin{array}{r}CH_3.CO\\H\end{array}\right\}O & \left.\begin{array}{r}C_2H_5.CO\\H\end{array}\right\}O
\end{array}$$

On the introduction of intermediate types these acids, as well as other compounds of conjugated radicals, were referred to them as follows:

$$\begin{array}{cccc}
\text{Type.} & \text{Formic Acid.} & \text{Acetic Acid.} & \text{Propionic Acid.} \\
\begin{array}{l}\left.\begin{array}{r}H\\H\end{array}\right\}\\\left.\begin{array}{r}H\\H\end{array}\right\}O\end{array} &
\begin{array}{l}\left.\begin{array}{r}H\\CO\end{array}\right\}\\\left.\begin{array}{r}\\H\end{array}\right\}O\end{array} &
\begin{array}{l}\left.\begin{array}{r}CH_3\\CO\end{array}\right\}\\\left.\begin{array}{r}\\H\end{array}\right\}O\end{array} &
\begin{array}{l}\left.\begin{array}{r}C_2H_5\\CO\end{array}\right\}\\\left.\begin{array}{r}\\H\end{array}\right\}O\end{array}
\end{array}$$

The followers of Berzelius, of whom Frankland and Kolbe are the most distinguished, held similar views, but not accepting at that time the new atomic weights nor the existence of radicals containing oxygen, they wrote their formulæ in a different way; thus Kolbe expressed the constitution of acetic acid by the formula, $HO.(C_2H_3)C_2,O_3$.

This short sketch of the theory of the types and conjugated radicals will be sufficient to show what influence it had on the progress of organic chemistry. A clear and complete exposition of them will be found in Kekulé's memoir: "Über die sogenannten gepaarten Verbindungen und die Theorie der mehratomigen Radicale,"* and in his "Lehrbuch der organischen Chemie."

One of the chief merits of Gerhardt's labours was the banishment of the old notions of radicals, as if they were rigid, almost unalterable bodies, which notion he replaced by that of residues, or groups of atoms, which, although like the remaining together during a certain number of chemical metamorphoses, are capable of being resolved by other changes into more simple fragments. By the development of the theory of types, light was thrown upon chemical facts from all sides, and analogies and contrasts were made strikingly apparent, which opened the way towards a general view of the remarkable deportment exhibited by the atoms in combinations or decompositions.*

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* Ann. Chem. Pharm. CIV., 129.

By going back from the radicals to the atoms, the foundation was laid of our present theory, which surpasses all previous ones by its surprising simplicity. Kekulé was the first who insisted upon this point in his memoir already mentioned, as well as in other papers and in his "Lehrbuch."

Even more pointedly A. S. Couper† showed that only by examining the properties of atoms we should be enabled to ascertain the manner in which they attract each other in a molecule.

An attempt towards this had already been made by Frankland‡ in 1852, when he said:—"When the formulæ of inorganic chemical compounds are considered, even a superficial observer is impressed with the general symmetry of their construction. The compounds of nitrogen, phosphorus, antimony, and arsenic, especially, exhibit the tendency of these elements to form compounds containing 3 or 5 atoms of other elements; and it is in these proportions that their affinities are best satisfied; thus in the ternal groups we have NO_3, NH_3, NI_3, NS_3, and in the five-atom group, NO_5, NH_4O, NH_4I, PO_5, PH_4I, &c.|| Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, *it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element*, if I may be allowed the term, *is always satisfied by the same number of these atoms.* It was probably a glimpse of the operation of this law amongst the more complex organic groups which led Laurent and Dumas to the enunciation of the theory of types; and had not these distinguished chemists extended their views beyond the point

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* Lothar Meyer, Modern. Theor., 150.

† Phil. Mag. (4) XVI., 104.

‡ Phil. Trans. CXLII., 417.

|| $O=8$; $S=16$.

to which they were well supported by then existing facts, had they not assumed that the properties of an organic compound are dependent upon the *position* and not upon the *nature* of its single atoms, that theory would undoubtedly have contributed to the development of the science to a still greater extent than it has already done."

Recently Frankland* has pointed out that: "This hypothesis constitutes the basis of what has since been called the doctrine of atomicity, or the equivalence of elements; and it was, so far as I am aware, the first announcement of that doctrine."

It was not only this; it was more; we find here an opinion pronounced which afterwards led to a most interesting controversy, *i.e.*, whether the atomicity of an element is constant or variable. The former opinion was held by the chemists of Gerhardt's school, of which Kekulé is the chief representative. It is easy to see that the theory of types must have led to the conception of a constant atom-fixing power; hydrogen and the halogens possessing one, oxygen and sulphur two, the elements of the nitrogen group three, and carbon and silicon four.

These typical elements were first distinguished like the compound radicals as being *monatomic*, *diatomic*, *triatomic*, and *tetratomic.*† However, these terms were soon found to be very inappropriate, inasmuch as we cannot well speak of a monatomic or diatomic, &c., atom. The word *atomicity* was therefore changed into *quantivalence* or *valency* (Chemischer Werth) and the above terms into *univalent*, *bivalent*, *trivalent* and *quadrivalent*,‡ which are still used in France,‖ while in Germany the corresponding words *einwerthig*, *zweiwerthig*, &c.,§ have been generally accepted, and in England Odling's¶ proposal to call them *monad*, *dyad*, *triad*, *tetrad*, has found general favour. The first two of these words were introduced into chemistry by

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* Experimental Researches, 1877, 145.

† The terms monatomic, &c., had been used much earlier but in a different and varying sense. Thus Berzelius, in 1827, called fluorine, chlorine, &c., polyatomic elements, because several atoms of them could combine with a single atom of another element. Gaudin de Saintes employed the same terms in 1833 in the sense in which they ought to be, and have since been used by Gmelin, Clausius, and Odling, *i.e.*, to express the number of atoms contained in a molecule; thus mercury forms a monatomic, oxygen a diatomic, and water a triatomic gas.—Lothar Meyer, Modern. Theor., 140.

‡ Zeitsch. Chem. Pharm., 1860, 540.

‖ A. Wurtz, La Théorie Atomique, 187.

§ Mod. Theor., 141.

¶ Tables of Chem. Form., 1864.

Laurent,* who however expressed by them something quite different. He called the elements which Odling designates as dyads (or diads) and tetrads, *monads*, because they could be added as a single atom, as in the conversion of aldehyde C_2H_4O into acetic acid $C_2H_4O_2$, while he called the monad and triad elements *dyads* because they could be added in pairs only, as in the conversion of ethene C_2H_4 into the dichloride $C_2H_4Cl_2$, &c.

In order to avoid confusion, Odling† has proposed to call the former *artiads* (ἄρτιος, even) and the latter *perissads* (περισσός, uneven). We cannot here discuss the interesting question whether the valency of an element is constant, as Kekulé maintained, defending his opinion most ingeniously, or is variable, as Frankland has always insisted upon. We refer those readers who take an interest in this subject to Lothar Meyer's "Moderne Theorien," last edition.

CHAPTER V.

COMPOUND RADICALS EXIST IN INORGANIC COMPOUNDS AS WELL AS IN ORGANIC SUBSTANCES.—ALL ORGANIC COMPOUNDS CONTAIN CARBON.—THIS ELEMENT DIFFERS FROM ALL OTHER ELEMENTS QUANTITATIVELY AND QUALITATIVELY.—ORGANIC CHEMISTRY DEFINED AS THE SCIENCE OF THE HYDROCARBONS AND THEIR DERIVATIVES.—HOMOLOGOUS SERIES.

We must interrupt our tale once more, and go back to the time when Williamson applied the theory of types to inorganic compounds. He showed that these, like organic bodies, contain compound radicals; it is true the existence of such was assumed before, but their number was very small, including ammonium, uranyl, and cyanogen, which latter was still classed by some chemists under the head of inorganic chemistry. But now they soon became so numerous that organic chemistry could no longer be defined as the chemistry of compound radicals.

The only difference now remaining between the two disciplines was exactly as it had heen the case at the time of Stahl and of Lavoisier, simply a qualitative one. All bodies formed in organic nature were found to contain carbon and hydrogen, the majority also oxygen, and many in addition to these nitrogen. In accordance with the older views it was still believed by some that the hydrogen in several cases existed in the form of water, as in oxalic acid, and consequently the only element which all organic compounds had in common was carbon, as Gerhardt first pointed out in 1846.

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* Chemical Method, 47.

† Phil. Mag., Feby., 1864.

Organic chemistry might therefore now have been defined as the chemistry of carbon-compounds, or of compound radicals containing carbon. But by such a definition, several compounds of this element, which always had been classed among inorganic ones, would now have become organic bodies, such as carbonic oxide, carbon oxychloride, carbon sulphide, the several then known chlorides of carbon and similar bodies, which are not found in the organic world, or others, such as carbon dioxide and marsh gas, which principally occur in the mineral kingdom.

Such a consequence however being shunned, several ways were tried to get over this difficulty. Thus Gmelin says in his handbook, 1848:

"Carbon is the only element which is essential to organic compounds. Every one of the other elements may be absent from particular compounds, but no compound, which in all its relations deserves the name of organic, is destitute of carbon.

"If we were to regard as organic those carbon compounds which have hitherto been classed among inorganic substances, viz., carbonic oxide, carbonic acid, sulphide of carbon, phosgene, cast iron, &c., we might define *Organic Compounds* simply as the *Compounds of Carbon.*

"But organic compounds are still further distinguished by containing more than one atom of carbon.

"Hence the term *Organic Compounds* includes all *Primary Compounds containing more than one atom of carbon.* By primary compounds we mean such as are not, like bicarbonate of potash, made up of other compounds."

In order to understand these definitions we must remember that Gmelin used the old equivalent weights, and therefore wrote with the majority of chemists:

Carbonic oxide CO Carbonic acid CO_2
Phosgene gas $COCl$ Sulphide of carbon CS_2

while to the most simple organic bodies the following formulæ were given:

Methyl alcohol $C_2H_4O_2$ Formic acid $C_2H_2O_4$
Hydrocyanic acid C_2NH Chloroform C_2HCl_3

However, as soon as Gerhardt's atomic weights were universally recognised, Gmelin's definition fell to the ground, and it was then said that organic chemistry was simply the chemistry of the carbon compounds. Kekulé, who first distinctly advocated this view, says in his excellent "Lehrbuch," which, as is much to be regretted, he has not completed:

"We have now come to the conviction that the chemical compounds found in the vegetable and animal kingdom contain the same elements as the bodies existing in inanimate nature; we are convinced that in the one the elements obey the same laws as in the other, and consequently that no difference exists between inorganic and organic compounds with regard to either the matter or the forces concerned, or the number and the arrangement of the atoms. We observe a continuous series of compounds, their single members (comparing only those which are placed near together) resembling each other so closely that no natural boundary can be traced anywhere. But if we want to do so, which indeed we must do for the sake of clearness, such a boundary is not a natural, but quite an arbitrary one, and therefore we may draw that boundary line wherever we find it convenient. If we retain the old division, it appears most convenient to place, as has already been done, all compounds of carbon together, and describe them in the part called organic chemistry.

"We define therefore *organic chemistry* as the *chemistry of the carbon compounds*. But this does not imply any real difference between inorganic and organic bodies. That part of our science to which the time-honoured name of *organic chemistry* is given, and which more conveniently we call the *chemistry of the carbon-compounds*, is only a special part of *pure chemistry*, treated separately on account of the large number and importance of the carbon compounds, by which a special study of them becomes necessary."

Other chemists expressed similar views; thus Erlenmeyer says: "that a division of labour is requisite in the interest of teaching." "Besides," he adds, "it cannot be denied that by reason of certain properties possessed by carbon, the carbon compounds exhibit several peculiarities in their chemical beahviour. Their study therefore requires in many respects peculiar methods of investigation, different from those employed in the study of the compounds of the other elements; and thus the necessity for a division of labour has also made itself apparent in the interest of scientific research."*

The great importance and the immense number of the compounds containing carbon were however given as principal reasons for describing them apart from, and after those, of the other elements; and although the definition of organic chemistry as that of the carbon compounds was considered as somewhat unnatural and not quite correct, it appeared at least to be very convenient.†

But such a separation of the carbon compounds from those of all the other elements has never been consistently carried out. No chemist ever thought of omitting the oxides, the sulphide, and other compounds of carbon from inorganic chemistry, or much less of placing soda-ash, calc-spar, spathose iron-ore, &c., amongst organic compounds.

When it was stated that organic compounds exhibited several peculiarities, which distinguish them from mineral bodies, no great advance had been made on Gmelin's stand point, who already, in 1815, had said that the difference existing between inorganic and organic bodies could be better felt than defined.

Therefore in looking over modern works on chemistry we find the oxides of carbon, carbon sulphide, phosgene gas, &c., mentioned in the inorganic as well as in the organic part, or sometimes several of them in the former and others in the latter. The same is the case with the cyanogen compounds, the simple reason being that these bodies, which contain only one atom of carbon, bear in many respects more resemblance to inorganic compounds than to the remainder of those generally described in organic chemistry.

On the other hand wood-spirit (methyl alcohol), formic acid, and other bodies, which also contain one atom of carbon in the molecule, have never been regarded as inorganic compounds, because they show the closest relationship to ethyl alcohol, acetic acid, and analogous bodies containing more carbon; indeed it was the peculiar behaviour of these latter bodies which gave rise to this division of pure chemistry into two parts.

The cause of these pecularities is not far to seek; carbon possesses certain characteristic properties by which it differs from all other elements.

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* Lehrbuch Org. Chem., 5.

† Butlerow. Lehrb. Org. Chem., 5.

If we examine all compounds which are products of organic life we find that, besides carbon, they invariably contain hydrogen; oxygen is also present in most cases, and in addition to these many contain nitrogen, while others consist only of carbon, hydrogen, and nitrogen.

Although composed of a small number of elements only, they are much more numerous than the compounds of all the other elements taken together. Moreover, the number of atoms forming a molecule is frequently very large; thus oil of turpentine, which is a hydrocarbon, contains 26, cane-sugar which consists of carbon, hydrogen, and oxygen, contains 45, and stearin, containing the same elements, even 173 atoms.

Kekulé,* who first showed that carbon is a tetrad element, pointed out at the same time that the existence of such an immense number of carbon compounds can be easily explained by assuming that the atoms of this element have the property of combining with each other. The same view was expressed by Couper.†

The same property is possessed by other polyvalent elements such as oxygen or sulphur, but while in the case of the latter elements the number of atoms uniting together is very limited, we have not yet found such a limit to exist in the case of carbon.

It is therefore most characteristic for tetrad carbon that a large number of its atoms can be linked together to form a group, which in a great many reactions remain together and act like a single atom.

But carbon possesses yet another property in common with no other element. *All the combining units in such a group, which are not saturated with carbon, can be saturated with hydrogen.*

We are therefore acquainted with a large number of hydrocarbons, their number increasing almost daily by the discovery of new ones; and all of them are volatile, while among the other elements only those of the chlorine group, oxygen group, nitrogen group, boron and silicon, form volatile hydrides, and each of them only one, with the exception of phosphorus, of which two are known.

The hydrocarbons are not only the most simple of the carbon compounds, but from a theoretical point of view also the most important, because all other carbon compounds can be regarded as derivatives of them, or as being formed by the substitution of other elements for hydrogen. This is shown by the fact that a very considerable number of vegetable and animal substances can be prepared artificially from hydrocarbons. On the other hand, as soon as the constitution of a carbon compound is clearly understood, we are in a position to convert it into the hydrocarbon, from which theoretically it has been derived.

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* Ann. Chem. Pharm. CIV. 129; Lehrb. I. 161.

† Phil. Mag. (4), XVI. 104.

In the majority of the carbon compounds occurring in nature, a portion of the hydrogen of the original hydrocarbon is replaced by oxygen, and in others by nitrogen, or in a few cases by sulphur; all the other elements can however be introduced artificially into carbon compounds. But there are only a few cases in which all the hydrogen can be replaced.

Thus the number of carbon chlorides is very much smaller than that of the hydrocarbons. With oxygen carbon forms only two compounds, and with nitrogen alone it unites only in one proportion. From this it follows that the great majority of carbon compounds contain hydrogen, and that there is present in them a residue of the original hydrocarbon.

We may therefore define organic chemistry as *the chemistry of the hydrocarbons and their derivatives.*[*]

But even this definition does not fix a definite boundary-line between inorganic and organic chemistry, because it can be easily shown that carbon dioxide, carbon sulphide, carbon oxychloride, hydrocyanic acid, and similar compounds, which we find described in works on inorganic chemistry, are, like methyl alcohol and formic acid, derivatives of the most simple hydrocarbon which we know, *i.e.*, marsh gas CH_4. If we burn it in air or oxygen, carbon dioxide and water are formed, four atoms of monad hydrogen being replaced by two of dyad oxygen.

Marsh gas cannot be converted directly into carbon sulphide, but the former can be obtained from the latter. By passing a mixture of the vapour of carbon disulphide and hydrogen sulphide over red-hot copper, marsh gas is formed:

$$CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S.$$

By the action of chlorine on marsh gas we obtain methyl chloride CH_3Cl, which when heated with caustic potash is converted into methyl alcohol:

$$CH_3Cl + KOH = CH_3.OH + KCl.$$

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[*] Schorlemmer, Carbon Compounds, 6.

On oxidising the latter we obtain formic acid CH_2O_2, one atom of oxygen being substituted for two of hydrogen.

By the continued action of chlorine on marsh gas we can replace one atom of hydrogen after the other by this element, the third product thus formed being chloroform, which when heated with ammonia is converted into hydrocyanic acid:

$$CCl_3H + 4NH_3 = CNH + 3NH_4Cl.$$

The three atoms of monad chlorine are thus replaced by one atom of triad nitrogen; but as all, even the most complicated cyanogen compounds, may be regarded as derivatives of hydrocyanic acid, they may also be considered as being derived from marsh gas. The same holds good for all the carbonates, or the salts of carbonic acid $CO(OH)_2$, which, although not known in the pure state, undoubtedly exists in the aqueous solution of carbon dioxide. We may even go further and regard the different kinds of cast iron and the carbides of other metals as derivatives of hydrocarbons, because, when we dissolve them in acids the metal, combined with the carbon, is replaced by hydrogen and hydrocarbons are formed.

There exists only one carbon compound of which the corresponding hydrocarbon is not known. This is the most simple of all, or carbonic oxide CO; all attempts which have been made to obtain the hydrocarbon methene CH_2 have been in vain.

Marsh gas is the only hydrocarbon containing one atom of carbon, but we know three with two atoms of carbon:

Ethane C_2H_6, Ethene C_2H_4, Ethine C_2H_2.

To explain the constitution of these we assume that in the first the two carbon atoms are linked together by one combining unit of each, in ethene by two, and in ethine (acetylene) by three; or the two carbon atoms in ethane form a hexad, in ethene a tetrad, and in ethine a dyad group.

In a similar manner three and more carbon atoms may be linked together. Thus, the above hydrocarbons form the initial members of three series, in which each member differs from the preceding one by containing one atom of carbon and two of hydrogen more. Their composition may therefore be expressed by the general formulæ:—

	C_nH_{2n+2}		C_nH_{2n}		C_nH_{2n-2}
Methane	CH_4	—		—	
Ethane	C_2H_6	Ethene	C_2H_4	Ethine	C_2H_2
Propane	C_3H_8	Propene	C_3H_6	Propine	C_3H_4
Butane	C_4H_{10}	Butene	C_4H_8	Butine	C_4H_6
Pentane	C_5H_{12}	Pentene	C_5H_{10}	Pentine	C_5H_8
Hexane	C_6H_{14}	Hexene	C_6H_{12}	Hexine	C_6H_{10}
&c.		&c.		&c.	

Besides these, others are known having the general formulæ C_nH_{2n-4}, C_nH_{2n-6}, &c. ; it is self-evident that the initial member of these must contain more than two atoms of carbon.

All other organic compounds are derived from these hydrocarbons by the substitution of other elements for hydrogen. Just as by the action of chlorine on marsh gas we obtain methylchloride, we can transform the other members of the series into chlorides of monad radicals. The chlorine in these can be replaced by hydroxyl OH, a series of hydroxides being formed called the alcohols* which have the general formula $C_nH_{2n+2}O$.

When methyl chloride is heated with ammonia it is converted into a powerful base, called methylamine :

$$CH_3Cl + NH_3 = CH_3.NH_2 + HCl.$$

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*The name alcohol was first given to spirits of wine, or ethyl alcohol, and then used as a generic term for the whole group. The origin of the word is not exactly known. In Arabic and Hebrew *kohl* is the name of native antimony sulphide, which, as an impalpable powder, has from early times been, and is still, used in the East for the painting of eye-brows and eye-lids. This custom we find mentioned in Ezekiel, and in the second Book of Kings. (See Kopp. Geschischte der Chemie IV., 100.) The Spaniards, who took many words from the Arabic, adopted this term, and in the Spanish Bible we find therefore the passage, in which Ezekiel mentions it, translated: "alcoholaste tus ojos."

In chemical literature the word is first found in the 16th century in the same sense, but at the same time as a generic term for any very finely divided powder, and still to-day iron-powder is called in pharmacy "ferrum alcoholisatum." But singularly enough the same name was also given to concentrated spirits of wine. Libavius says in his Alchymia, 1595 : "*Quando vini spiritus rectificatur per suum salem* (potassium carbonate obtained by calcining tartar) *seu potius exasperatur, nominant vini alcool, vel vinum alcalisatum.*" Johnson's Lexicon Chymicum, 1657, gives the following explanations : "*Alcohol est antimonium sive stibium. Alcohol, vini, quando omnis superfluitas vini a vino separatur ita ut accensum ardeat, donum totum consumatur, nihilque fœcum aut phlegmatis in fundo remaneat.*" The passage quoted from Libavius seems to point out that strong spirits of wine was originally called vinum alcalisatum, or wine strengthened by means of an alkali, and that by some mistake this was then written vinum alcoholisatum, a term which was also used, and was then converted into alcohol vini (Kopp. loc. cit. IV., 279).

By the same reaction the other chlorides of the alcohol radicals are transformed into such amines or bases of the general formula $C_nH_{2n+3}N$. When methyl alcohol is oxidised, it is converted into formic acid, two atoms of hydrogen being replaced by one of oxygen; in the same way all other alcohols of the series $C_nH_{2n+2}O$ yield acids of the general formula $C_nH_{2n}O_2$, which, as most of them occur in oils and fats, have been named the fatty acids.

The hydrocarbons of the marsh gas series yield therefore the following groups of derivatives:

Chlorides.		Alcohols.	
Methyl chloride	...CH_3Cl	Methyl alcohol	...CH_4O
Ethyl chloride	......C_2H_5Cl	Ethyl alcohol	......C_2H_6O
Propyl chloride	...C_3H_7Cl	Propyl alcohol	......C_3H_8O
Butyl chloride	......C_4H_9Cl	Butyl alcohol	......$C_4H_{10}O$
Pentyl chloride	...$C_5H_{11}Cl$	Pentyl alcohol	......$C_5H_{12}O$
Hexyl chloride	......$C_6H_{13}Cl$	Hexyl alcohol	......$C_6H_{14}O$
&c.		&c.	

Amines.		Fatty Acids.	
Methylamine	......CH_5N	Formic acid	.........CH_2O_2
Ethylamine	.........C_2H_7N	Acetic acid	.........$C_2H_4O_2$
Propylamine	......C_4H_9N	Propionic acid	......$C_3H_6O_2$
Butylamine	.........$C_4H_{11}N$	Butyric acid	.........$C_4H_8O_2$
Pentylamine	......$C_5H_{13}N$	Valerianic acid	.....$C_5H_{10}O_2$
Hexylamine...	.....$C_6H_{15}N$	Caproic acid	.........$C_6H_{12}O_2$
&c.		&c.	

Besides these, many other derivatives are known, which all can be arranged in such series; and exactly the same we find to be the case with derivatives of other series of hydrocarbons.

All hydrocarbons contain an even number of hydrogen atoms, which is a consequence of carbon being a tetrad element. From this it follows that the sum of the number of perissads contained in a carbon compound must always be an even number, while that of the artiads is not thus restricted.

When Laurent, in 1836, brought forward his nucleus theory, he already arranged the organic compounds in series, but J. Schiel* first pointed out, in 1842, that "the radicals of the bodies called alcohols formed not only a most simple and regular series, but that their properties exhibit a corresponding regularity."

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* Ann. Chem. Pharm., XLIII. 107.

He then gives the following arrangement ($C = 6$):

If the hydrocarbon compound C_2H_2 be called R, we have :

$R_1\,H$ = Methyl.
$R_2\,H$ = Ethyl.
$R_3\,H$ = Glyceryl.
$R_4\,H$ = ?
$R_5\,H$ = Amyl.
$R_{16}H$ = Cetyl.
$R_{24}H$ = Cerosyl.

He further said that undoubtedly other organic compounds might be arranged in similar series. Dumas* very soon afterwards showed that the fatty acids form such a group, and that their physical properties, as in the case of the alcohols, vary regularly with their composition.

C. Gerhardt, in 1843, and in his "Précis de Chimie Organique" (1844 and 1845), arranged then a number of organic compounds in such *homologous* series, as he called them; on the other hand, compounds derived from each other by simple reactions, such as ethyl chloride, ethylamine, ethyl alcohol, acetic acid, &c., he named *heterologous* compounds.

Such a classification in homologous and heterologous series he compared ingeniously with a pack of cards which are arranged in such a way that all cards of the same value are placed in horizontal and all of the same colour in vertical rows, the former corresponding to the homologous and the latter to the heterologous series. If a card is missing, we know its place, its colour, and its value. The same holds good if members of a homologous series are wanting: we know not only their composition and principal properties, but we also can find ways and means of preparing them, and thus complete the series.

The existence of homologous series is particularly characteristic of the carbon compounds. The *chemical character* of the different series of hydrocarbons depends on *the manner in which the carbon-atoms are linked together*, whilst the *physical properties* of each member depend on the *number of carbon-atoms* which it contains. Thus we find that the initial or lower members are often gases or very volatile liquids, the boiling point increasing with the increase of carbon, the higher members being generally solids. They nevertheless all resemble each other in their chemical properties.

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* Compt. Rend. XV. 935.

If we now, in all the members of such a group of hydrocarbons, replace hydrogen by elements or compound radicals, we obtain homologous series, the members of which, as might be expected, possess a very similar chemical character, but varying physical properties.

A consequence of this is, that whilst the proportionally limited number of the compounds of other elements allows us to elucidate the nature and composition of a substance by a few reactions, this is generally not the case with the carbon compounds; only a very limited number can be recognised by qualitative analysis. In most cases it is necessary to obtain the compound to be examined in a perfectly pure state, and to find its exact composition by quantitative analysis, or, as it is also called, ultimate analysis, because the quantity of each element present in the compound must be determined.

The improvements made in this branch of analytical chemistry went therefore hand in hand with the progress of our science.

CHAPTER VI.

Organic Analysis.—Calculation of Formula.—Determination of Molecular Weight.—Rational Formulæ.—The Law of the Linking of Atoms.—Graphic Formulæ.

It has already been mentioned that Berzelius, by employing a more exact method than those previously in use, succeeded in proving that organic compounds follow the laws of constant and multiple proportions. His process required however not only great practice, but also much time. Besides, it contained certain sources of error which could only with difficulty be avoided.

It is the great merit of Liebig that he, after six years' work, found a method which, although it has since been modified and improved, remains in principle the same, and allows us to determine carbon and hydrogen with the greatest exactitude.* Only then it became possible to analyse with ease a very large number of known bodies and of newly discovered ones. The determination of the composition of these bodies was of course only a stepping-stone for the brilliant researches of our great master and his pupils, which made the little university of Giessen famous throughout the civilised world.

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* Handwörterbuch, 1st ed., I. 357.

Liebig also designed new methods for the determination of nitrogen; one of these was then improved by Dumas and brought into its present shape by other chemists, while another method, although not applicable in all cases, but distinguished by its rapidity and simplicity, was worked out by Liebig's pupils, Varrentrapp and Will.

From the results of an analysis we can easily calculate the percentage composition of a compound; but only in very simple cases, when the number of atoms in a molecule is but small or their numerical relations are very simple, we can calculate the proportions in which the different atoms are combined. Generally this is however not the case, as the following simple example will show. The analysis of a hydrocarbon gave the following percentage composition:

Carbon	83·8
Hydrogen	16·3
	100·1

If we divide these numbers by the respective atomic weights, we find:

$$83{\cdot}8 : 12 = 6{\cdot}98.$$
$$16{\cdot}3 : 1 = 16{\cdot}30.$$

From this we see that the hydrocarbons belong to the series of the paraffins, having the general formula C_nH_{2n+2}. Its percentage composition comes nearest to that of hexane $C_{12}H_{14}$, but does not differ much from that of heptane C_7H_{16} or octane C_8H_{18}, as the following calculated percentage-composition shows:

	Hexane.	Heptane.	Octane.
Carbon	83·72	84·00	84·21
Hydrogen	16·28	16·00	15·79

Now, as in organic analysis the carbon is generally found a little too low and the hydrogen somewhat too high, owing to unavoidable experimental errors, we might be inclined to regard the compound as being most probably heptane, but the possibility that it is octane is also not excluded. Moreover, the substance may have contained small admixtures of other hydrocarbons, and consequently all we can say is that it belongs to the series of the paraffins.

In still more complicated cases we are quite at a loss to calculate a formula from the analytical results. Thus, a number of analyses of a colouring matter called aurin gave the following figures, which agree with each other as nearly as can be expected:

	(1)	(2)	(3)	(4)
Carbon......	78·79	78·48	78·61	78·42
Hydrogen...	5·00	5·06	4·91	4·89
Oxygen.....	16·21	16·46	16·48	16·69
	100·00	100·00	100·00	100·00

The reason that these figures all add up exactly to 100 is owing to the fact that we have no method for a direct determination of oxygen, and its percentage can only be found by difference, after all other elements present have been exactly determined.

From the above figures we can calculate a number of formulæ; of these it will be sufficient to give the following three and their calculated percentage composition:

	$C_{13}H_{10}O_2$	$C_{19}H_{14}O_3$	$C_{25}H_{18}O_4$
Carbon	78·79	78·62	78·53
Hydrogen......	5·05	4·83	4·72
Oxygen.........	16·16	16·35	16·75
	100·00	100·00	100·00

If, however, we can ascertain the molecular weight of a compound, we have no difficulty to make out its molecular formula. When a substance is volatile without decomposition, its molecular weight is readily found by determining its vapour density, *i.e.*, how many times its vapour is heavier than an equal volume of hydrogen at the same temperature and under the same pressure. This number multipled by two gives, according to Avogadro's law, the molecular weight of the compound.

For workers on the field of the carbon compounds it is, therefore, next to being well acquainted with the methods of ultimate analysis, of the highest importance to be in the possession of methods by which the vapour density of a body can be determined in an exact, quick, and simple manner.

Not long ago two methods were in use; one of these had been worked out by Gay-Lussac and the other by Dumas. But in the course of time it was found that they were not sufficient for the progress of science, inasmuch as that of Gay-Lussac could only be employed with advantage for substances boiling below 100°, whilst that of Dumas, which was not thus restricted, had the great drawback that the greater part of the material was wasted, being used to drive the air out of the apparatus. This became a serious consideration in the case of valuable preparations.

Efforts have therefore repeatedly been made to improve or modify these old methods. Of these, that of Hofmann was first crowned with success. His process soon superseded the older ones, and has since been improved by him and others.* Quite recently V. Meyer had added to it other methods, distinguished by their elegance and simplicity.†

If we know the percentage composition of a carbon compound and its molecular weight, we are, in most cases, able to find its molecular formulæ. Yet still difficulties may arise in some cases. Thus, two very similar hydrocarbons were found to have the following composition :

	(*a*)	(*b*)
Carbon	94·1	93·8
Hydrogen	5·9	6·3
	100·0	100·1

The determination of the vapour density gave as result, that the molecular weight of (*a*) is 180 and that of (*b*) 189. If we now calculate how much carbon and hydrogen is contained in these parts of weight, we find :

	(*a*)	(*b*)
Carbon	169·4	177·3
Hydrogen	10·6	11·7
	180·0	189·0

On dividing these numbers by the atomic weights of the elements we find :

	(*a*)	(*b*)
Carbon atoms	14·1	14·74
Hydrogen atoms	10·6	11·70

From these numbers it appears probable that (*a*) has the molecular formula $C_{14}H_{10}$, and (*b*) is perhaps its next homologue $C_{15}H_{12}$, although the numbers found do not well agree with this formula. But this is partly accounted for by the fact that, in the above calculations, all the errors made in the analysis and vapour density determination have accumulated. They may however be separated again by calulating the percentage composition and vapour density required by theory, and comparing these numbers with those found by experiment:

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* Ber. Deutsch. Chem. Ges., I. 198 ; IX. 1304.

† Ibid. IX. 1216 ; X. 2068 ; XI. 2253.

	(a)			(b)	
	Calculated.	Found.		Calculated.	Found.
Carbon	94·38	94·1	...	93·75	93·8
Hydrogen	5·62	5·9	...	6·25	6·3
	100·00	100·0	...	100·00	100·0
Vapour density	178	180	...	192	189

Now the calculated numbers agree with those found by experiment within the limits of unavoidable errors; we may therefore safely assume that the above formulæ are correct, which has also been proved by studying the chemical metamorphoses of the two hydrocarbons (*a*) being anthracene and (*b*) methylanthracene, one atom of hydrogen in the former being replaced by methyl.

In some cases we can ascertain the molecular formula of a compound in a very simple way, namely, if we know to which homologous series the body belongs. Thus, a hydrocarbon of the marsh gas group can be readily distinguished from all others, by being not acted upon in the cold by concentrated nitric or sulphuric acid, or a mixture of both. For this reason these hydrocarbons have been called the paraffins (*parum affinis*), a name which was first applied to the higher solid members, and subsequently, on the proposal of Henry Watts, extended to the whole series. If we want to find the molecular formula of a paraffin, it is only necessary to determine its vapour density; thus the molecular weight of the compound which was analysed with the results above given was found 99·3. From this we calculate the number of carbon atoms as follows:

$$12n + 2n + 2 = 99{\cdot}3.$$
$$n = 6{\cdot}96.$$

It is therefore heptane C_7H_{16} which has the molecular weight 100.

It often happens that in certain oxidations we obtain acids belonging, as we know beforehand, to a known series, such as that of the fatty acids. If we are able to obtain these in the pure state, we readily ascertain their molecular formulæ by determining the quantity of a metal contained in a given weight of an anhydrous normal salt. The silver salts, which can be easily obtained pure, and generally do not contain water of crystallisation, are preferred for this purpose, as by simply igniting the salt, pure silver is left behind.

On analysing such a salt it was found to contain 51·4 % silver; from that we calculate the molecular weight of the salt by the following equation:

$$51{\cdot}4 : 100 = 107{\cdot}7 : x$$
$$x = 209{\cdot}4.$$

The silver salt differs from the acid by containing one atom of silver in the place of one atom of hydrogen; consequently the molecular weight of the acid is

$$(209{\cdot}4 - 107{\cdot}7) + 1 = 102{\cdot}7.$$

The general formulæ of the fatty acids being $C_nH_{2n}O_2$, we find n by the equation

$$\frac{102{\cdot}7 - 32}{14} = 5.$$

The acid is consequently valerianic acid $C_5H_{10}O_2$.

In the case of a compound ammonia or amine of a known series, such as $C_nH_{2n+3}N$, we proceed in a similar way; their hydrochlorides combine like salammoniac with platinic chloride, forming double salts of the general formulæ $(C_nH_{2n+3}N, HCl)_2PtCl_4$, which on ignition leave pure platinum behind. We readily find, therefore, the molecular weight of the base from the quantity of the metal thus obtained, and from this we can without difficulty deduce its molecular formula.

In many cases however we do not know to which group the body belongs, and, if it is not volatile, we must, in order to ascertain its formula, study its chemical properties. If it is an acid we try to find whether it is monobasic or polybasic, and analyse several of its salts; if we have a basic compound we may proceed in a similar way, and are thus, in most cases, enabled to fix its molecular formula, if not always with absolute certainty, yet generally with great probability. This may also be done by converting the body by simple reactions into compounds of known molecular formulæ or obtaining it from such. Such is generally the mode of proceeding, if the substance is neither an acid nor a base, and does not form well-defined compounds with other bodies, as, for instance, the different kinds of sugar.

Cane-sugar consists of:

Carbon	42·1
Hydrogen	6·4
Oxygen	51·5
	100·0

From these figures we can calculate a number of formulæ, just as in the case of aurin. If we boil cane-sugar with dilute sulphuric acid, it yields equal weights of grape-sugar or dextrose, and fruit-sugar or levulose, which differ chiefly by their optical properties, the former turning the plane of polarisation to the right and the latter to the left, while they have an identical composition and the same chemical character. They contain in 100 parts:

Carbon	40·0
Hydrogen	6·6
Oxygen	53·4
	100·0

If we divide these numbers by the atomic weights of the elements, we find:

$$40{\cdot}0 : 12 = 3{\cdot}3$$
$$6{\cdot}6 : 1 = 6{\cdot}6$$
$$53{\cdot}4 : 16 = 3{\cdot}3$$

They contain, therefore, for each atom of carbon and each of oxygen 2 atoms of hydrogen, or their most simple formula is CH_2O; but this cannot represent the molecule, because such a simple body would be readily volatile, whilst the sugars are completely decomposed by heat, a fact pointing to their having a high molecular weight, which weight however remains so far undecided.

If we divide the percentage numbers of cane-sugar by the atomic weights of its elements, we get the following results:

$$42{\cdot}1 : 12 = 3{\cdot}5$$
$$6{\cdot}4 : 1 = 6{\cdot}4$$
$$51{\cdot}5 : 16 = 3{\cdot}2$$

From these we see that it contains, like the two other sugars, two atoms of hydrogen for each atom of oxygen, but in proportion more carbon, pointing out that in the formation of these two sugars, cane-sugar has taken up the elements of water, but how much we cannot ascertain from the results of the analysis.

Now, both grape-sugar and fruit-sugar are by fermentation resolved into equal molecules of ethyl alcohol C_2H_6O and carbon dioxide CO_2, from which it appears that their molecular formula cannot be smaller than $C_3H_6O_3$. Assuming this formula, we can easily calculate how much hydrogen and oxygen are in cane-sugar combined with three atoms of carbon; on doing it we find the formula of the latter to be $C_3H_{5 \cdot 5}O_{2 \cdot 75}$. But as the number of the hydrogen atoms must be even, the molecular formula of cane-sugar must be $C_{12}H_{22}O_{11}$ or a multiple. If we take the former to be the case, the formation of the two other sugars is easily explained by the following equation:

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

Other facts point to the same conclusions. Thus Liebig* has shown that when a solution of sugar is gently heated with pure potassium permanganate, these compounds are converted into normal potassium oxalate, manganese dioxide and water, according to the equation:

$$C_{12}H_{22}O_{11} + 12KMnO_4 = 6K_2C_2O_4 + 12MnO_2 + 11H_2O.$$

Yet, we have no positive proof that the above formulæ represent the molecule, but this becomes very probable for the following reasons:

Manna contains a crystalline solid, which is nearly related to the sugars and has been called mannite. It appears therefore probable that its molecule contains either 6 or 12 atoms of carbon; its formula as deduced from the results of analysis might therefore be either $C_6H_{14}O_6$, or $C_{12}H_{28}O_{12}$. The latter is however quite inadmissible, because no carbon compound can contain more hydrogen than a paraffin, the limit being C_nH_{2n+2}; consequently the first of these formulæ is given to mannite, and that it represents its molecule is shown by the fact that it can easily be converted into hexane C_6H_{14}. Indeed it is a derivative of this hydrocarbon containing, in the place of 6 atoms of hydrogen, six hydroxyls $C_6H_8(OH)_6$. From this it further follows that grape-sugar and fruit-sugar have the molecular formula $C_6H_{12}O_6$, because both combine with hydrogen in the nascent state, and are thereby converted into mannite.

As a last example for illustrating the methods we employ for ascertaining the molecular formula of a non-volatile compound, we will take aurin, of which the analysis has already been given.

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* Handwörterb. 1st ed., I. 395.

This body is formed by the action of oxalic acid $C_2H_2O_4$ on phenol C_6H_6O, the products consisting of aurin, formic acid $C_2H_2O_2$ and water. Now, as oxalic acid itself readily splits up into formic acid and carbon dioxide, it may be assumed that the latter in the nascent state acts on phenol according to the equation:

$$3C_6H_6O + CO_2 = C_{19}H_{14}O_3 + 2H_2O.$$

None of the other formulæ which may be deduced from the analytical results can be brought into accordance with the observed facts; moreover, it has been shown that aurin can readily be converted into the hydrocarbon $C_{19}H_{16}$, from which it is derived, by the replacement of two atoms of hudrogen by one of oxygen, and two others by two hydroxyls.

It has already been stated that Laurent and Gerhardt, in order to keep chemistry free from all fictions, used for some time only unitary or *empirical* molecular formula, which merely express the number of atoms constituting a molecule. But this attempt was soon given up again; it was found necessary to employ *rational* formulæ. By this term, introduced by Berzelius, we mean such formulæ as express the chemical constitution of a compound, *i.e.*, show its relations to other bodies, or its past and future. A body, as it exists, has only a subordinate interest for the theoretical chemist, who wants to know by what chemical metamorphoses it can be obtained from, or transformed into, other compounds.

It is obvious that in describing a body all its physical properties must be mentioned, as we require them for recognising the substance again, and as they serve as a criterion of its purity.*

But the study of these does not strictly belong to pure chemistry, and the time will not be far distant when they are treated together with mineralogy as a peculiar branch of science.

We have already seen how rational formulæ changed with the progress of chemistry, and that the adherents of the theory of types did not regard their rational formulæ as constitutional formulæ or such as express the relative position of the atoms in the molecule. They only intended to express by them in a concise way the different chemical changes which the body may undergo. But as all their metamorphoses could not be explained by one rational formula, a compound might have more than one of them.

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* Kekulé, Lehrb. I. 4.

These views were still pronounced by Kekulé in 1861, and yet he had already clearly pointed out two theses, on which our present theory is founded. He showed that carbon is a tetrad element, and that the immense number of its compounds can be easily explained by assuming that the atoms of this element possess the property of combining with each other. A little later Couper expressed similar views, perhaps even more pointedly than Kekulé, but undoubtedly not knowing the memoir of the latter. Thus he says: "This body (carbon) is found to have two highly distinguishing characteristics:—

"(1) It combines with equal numbers (equivalents) of hydrogen, chlorine, oxygen, sulphur, &c.

"(2) It enters into chemical union with itself.

"These two properties, in my opinion, explain all that is characteristic of organic chemistry."

From these views our present *law of the linking of atoms* has been developed, according to which the different atoms contained in a compound are not kept together, as was formerly supposed, by each attracting all the others, or a certain number of them, which exert a reciprocal attraction on it and keep it in its place, but that the attraction acts only from atom to atom; each is linked to the next, and this again to the following, just as in a chain link is joined to link; none can be removed without breaking the whole.

The links of such a chain do not consist of equivalent atoms; a monad may be compared with a link having only one hasp, a dyad possesses two, a triad three, and a tetrad four of them.

We will now see how by this theory the constitution of different carbon compounds may be explained. Kekulé has pointed out that if two carbon atoms combine, the most simple and therefore the most probable case is, that one combining unit* or bond, as Frankland calls it, enters into combination with one combining unit of the other atom; the group C_2 is therefore a hexad and can combine with six atoms of hydrogen to form the hydrocarbon ethane C_2H_6. When more than two carbon-atoms are linked together, they may combine in a similar manner, one fourth of the combining power of one atom being saturated by one fourth of the other, and thus the valency of the group is for each carbon-atom, entering it, increased by two units. Consequently the number of free combining units is expressed by the formula:

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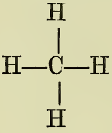
* Odling proposes the term *adicity* (ἀδέω, to be satisfied): thus in chloroform $CHCl_3$ the tetradicity of the carbon is $\frac{3}{4}$ satisfied by chlorine and $\frac{1}{4}$ by hydrogen.

$$2 + n(4 - 2) = 2 + 2n.$$

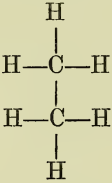
If we combine these groups with hydrogen we obtain the homologous series of the paraffins C_nH_{2n+2}, and their constitution can be explained by the following graphic formulæ:

Methane.



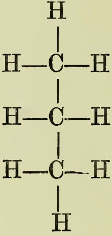
$$\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H \end{array}$$

Ethane.



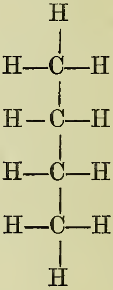
$$\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H—C—H \\ | \\ H \end{array}$$

Propane.



$$\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H—C—H \\ | \\ H—C—H \\ | \\ H \end{array}$$

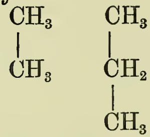
Butane.



$$\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H-C—H \\ | \\ H—C—H \\ | \\ H—C—H \\ | \\ H \end{array}$$

&c.,

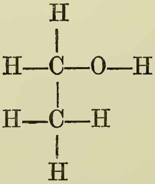
or more simply:



$$\begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} \qquad \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

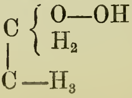
or $H_3C - CH_3$, &c.

By replacing in these hydrocarbons one atom of hydrogen by monad elements or groups, we obtain the compounds of the alcohol radicals; the graphic formula of ethyl alcohol, for instance, may be written thus:



$$\begin{array}{l} \quad\;\; H \\ \quad\;\;\; | \\ H—C—O—H \\ \quad\;\;\; | \\ H—C—H \\ \quad\;\;\; | \\ \quad\;\; H \end{array}$$

Similar formulæ were already employed by Couper, with the only difference that he assumed the atomic weight of oxygen to be 8, but that always two atoms of this bivalent element were combined together in organic compounds, and he wrote therefore the graphic formula of alcohol thus:



$$\begin{array}{l} C\left\{\begin{array}{l} O—OH \\ H_2 \end{array}\right. \\ | \\ C—H_3 \end{array}$$

The graphic formulæ which Kekulé used, but only exceptionally, in his Lehrbuch, are different from these.

Other chemists, who developed the law of the linking of atoms wrote such graphic, structural, or dissected formulæ, as they have been called, in different other ways. Some made afterwards claims of priority, but hardly with any justification. Lothar Meyer* has justly remarked that as soon as it was ascertained that the atoms of tetrad carbon can combine with each other, the arrangement of such formulæ became a very simple task. It is quite a matter of taste or convenience whether we write the series of symbols by which we express the linking of atoms, according to the use of Western Europe, from the left to the right, or in the opposite direction, as the Hebrews do, or from the top to the bottom, as the Chinese are accustomed to.

For lecture and class illustration, solid diagrams are often used, consisting of wooden balls of various colours, to represent the atoms, having holes for the insertion of connecting rods, which Kekulé first proposed. These representations are called *glyptic* formulæ. Already Dalton employed for illustrating his theory a kind of glyptic formulæ; but as his atoms were at the same time equivalents, he represented them simply by cubical blocks of wood of different colours.

Eminent chemists have made objection to the use of such illustrations, on the ground that it might lead the pupils to believe that atoms had that shape, or were thus arranged in space, and connected by material bonds. It is true that this may be the case. In fact a dunce, when asked to explain the atomic theory, answered, "Atoms are square blocks of wood, invented by Dr. Dalton."

But we might as well object to the use of diagrams or models for illustration of the parallelogram of forces, or, as Henry Watts† says, "to that of an artificial globe in teaching geography and astronomy, lest the student should acquire curious notions about the *brazen* meridian or *wooden* horizon."

Graphic and glyptic formulæ are of course hardly needed for explaining the constitution of the more simple carbon compounds. But they are of value in the case of more complicated ones, and principally for illustrating the different constitution of numerous compounds having the same percentage composition, but very different properties.

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[*] Ann. Chem. Pharm., CXLV. 124.

[†] Fownes' Chemistry, 12th ed., I. 258.

CHAPTER VII.

METHODS FOR DETERMINING THE CONSTITUTION OF COMPOUNDS.—THE HISTORY OF LACTIC ACID.—ISOMERISM.

We must now next explain, by some simple examples, what means we have to ascertain the constitution of a compound.

Ethyl alcohol C_2H_6O is a derivative of ethane and can, as Frankland has shown, be easily converted into this hydrocarbon. On heating it with hydriodic acid we obtain ethyl iodide:

$$C_2H_6O + HI = C_2H_5I + H_2O$$

If we heat this compound with zinc and water under pressure, we obtain ethane:

$$C_2H_5I + H_2O + Zn = C_2H_6 + Zn\left\{\begin{array}{l} I \\ OH. \end{array}\right.$$

On the other hand, by the action of chlorine on ethane we get ethyl chloride:

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl.$$

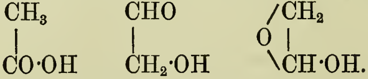
This chloride yields again the alcohol when heated with potash:

$$C_2H_5Cl + KOH = C_2H_5.OH + KCl.$$

Alcohol is therefore derived from ethane by replacing in the latter one atom of hydrogen, by the monad radical hydroxyl OH.

By oxidation alcohol is converted into acetic acid $C_2H_4O_2$, one atom of oxygen being substituted for two of hydrogen. The question now arises which of the six hydrogen atoms have been thus replaced; this, however, becomes limited by the fact that acetic acid, like alcohol, contains the group hydroxyl, as can be proved in different ways. Thus almost all carbon compounds containing this group, readily exchange it for chlorine when acted upon with phosphorus chloride, alcohol being converted into ethyl chloride, and acetic acid into acetyl chloride C_2H_3OCl.

From this it is clear that the constitution of acetic acid must be expressed by one of the following abridged graphic formulæ:



$$\begin{array}{l} CH_3 \\ \mid \\ CO{\cdot}OH \end{array} \qquad \begin{array}{l} CHO \\ \mid \\ CH_2{\cdot}OH \end{array} \qquad \begin{array}{l} \;/CH_2 \\ O\;\mid \\ \;\backslash CH{\cdot}OH. \end{array}$$

To decide among these, we have two general methods; we either split up the molecule into fragments, in order to obtain more simple compounds of known constitution, or we build it up from residues of such.

On heating acetic acid with an excess of an alkali, it is resolved into carbon dioxide and marsh gas:

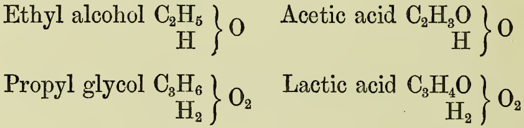
$$C_2H_4O_2 = CH_4 + CO_2.$$

By electrolysis acetic acid is decomposed into hydrogen, carbon dioxide, and methyl CH_3, which latter cannot exist in the free state, and therefore two of such imperfect molecules combine to form ethane. These decompositions make it highly probable that in acetic acid one carbon atom is directly combined with oxygen only, and the second with hydrogen. Its constitution would therefore be expressed by the first of the above formulæ. This is proved by the fact that we can obtain acetic acid synthetically from marsh gas, in which we can indirectly replace one atom of hydrogen by the monad radical cyanogen. If we heat the methyl cyanide thus obtained with a solution of caustic potash, we obtain ammonia and potassium acetate:

$$CH_3.CN + HOH + HOK = NH_3 + CH_3.CO.OK.$$

We can therefore express the constitution of acetic acid by the contracted graphic formula $CH_3.CO.OH$, which bears great resemblance to those used by Berzelius and by the adherents of the theory of types. But while the former understood by it that acetic acid was oxalic acid conjugated to methyl, and the latter that the dyad radical carbonyl could combine with the monad methyl, and the group $CO.CH_3$ thus formed could replace one atom of hydrogen in water, we mean now by our more or less dissected formula, that acetic acid contains two atoms of carbon linked together by one combining unit of each, and that the three other combining units of one atom are saturated with hydrogen, and those of the second with oxygen in two different ways, one atom of the latter being linked to carbon by both its combining units and the second by only one, the other bond of oxygen being combined with hydrogen, a closed molecule being thus formed.

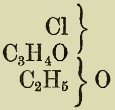
Another instructive example is offered by lactic acid, because it clearly shows how the theory of the types gradually changed into that of the linking of atoms. Lactic acid was discovered by Scheele in sour milk; Berzelius afterwards found it in several animal juices, and Mitscherlich as well as Liebig examined it more fully and determined its composition. Strecker obtained it then by a synthetical method which will be described further on; but its constitution, and even its molecular formula, remained doubtful, until Wurtz found that it could be formed by the oxidation of propyl glycol, the alcohol of the dyad radical propylene. As this reaction is perfectly analogous to the formation of acetic acid from common alcohol, Wurtz expressed the relations existing between these bodies by the following typical formulæ:



$$\text{Ethyl alcohol } \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O \qquad \text{Acetic acid } \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$$

$$\text{Propyl glycol } \left.\begin{matrix}C_3H_6\\H_2\end{matrix}\right\}O_2 \qquad \text{Lactic acid } \left.\begin{matrix}C_3H_4O\\H_2\end{matrix}\right\}O_2$$

As acetic acid is monobasic, Wurtz* concluded that lactic acid was bibasic; this view appeared to be confirmed by the fact that, by the action of phosphorus chloride, it is converted into lactyl dichloride $C_3H_4OCl_2$. On treating this compound with alcohol Wurtz obtained the so-called chlorolactic ether



$$\left.\begin{matrix}Cl\\C_3H_4O\end{matrix}\right\}\left.\begin{matrix}\\C_2H_5\end{matrix}\right\}O$$

Kolbe† opposed these views; he did not regard propylglycol as an alcohol of a dyad radical, but as a hydrate of oxypropylene $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}CO.H_2O$ and lactic acid as oxypropionic acid $C_2\left\{\begin{matrix}H_4\\OH\end{matrix}\right\}CO.OH$ or as propionic acid (which is oxalic acid conjugated with ethyl) in which one atom of hydrogen is replaced by hydrogen peroxide (hydroxyl)‡

He gives different reasons for proving his views, and explains from his standpoint the constitution of the compounds described by Wurtz. Thus lactyl dichloride he regards as the chloride of chloropropionic acid, and the ethyl compound obtained from it is chloropropionic ether. At the same time, he supports his theory by experimental proofs, and shows that by replacing the chlorine in the ether by hydrogen, propionic ether (ethyl propionate) is formed, and that lactic or oxypropionic acid is monobasic, like propionic acid.

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* Compt. rend. XLVI., 1228.

† Ann. Chem. Pharm. CIX., 257.

‡ Kolbe, who used equivalent formulæ, wrote these compounds thus:—propylglycol $\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}C_2O_2.2HO$, and lactic acid $HO.\left(C_4\left\{\begin{matrix}H_4\\HO_2\end{matrix}\right.\right)C_2O_3$.

But under certain conditions two atoms of hydrogen in lactic acid may be replaced by metals, and the existence of such salts furnished Wurtz* with a new argument for the correctness of his views. Moreover, he showed that lactic acid forms, besides the monethyl ether, also a diethyl compound, which, as has been mentioned, Gerhardt considered to be a chief characteristic of a bibasic acid.

Kolbe was not slow to reply; Lautemann had shown in Kolbe's laboratory that by the action of hydriodic acid on lactic acid, the group hydroxyl is replaced by hydrogen, propionic acid being formed, and Kolbe himself found that by the action of ammonia on chloropropionic acid the latter is converted into alanine or amidopropionic acid, which Strecker had already obtained synthetically from aldehyde and hydrocyanic acid, and which by treatment with nitrous acid is converted into lactic acid.†

Kolbe's views certainly agreed better with the facts than those of Wurtz, but the former overlooked the near relation between propyl glycol and lactic acid, and would not acknowledge that this glycol was an alcohol of a dyad radical.

Meanwhile Wurtz had made another step in advance, and now pointed out the distinction between basicity and atomicity (valency of its radical) of an acid. The facility with which hydrogen is exchanged for a metal does not only depend on the number of the extra radical hydrogen-atoms which an acid contains, but also on the nature of the radical. The basicity increases with the increase of oxygen :—

$$\begin{array}{ccccc} \text{Ethyl Glycol.} & & \text{Glycollic Acid.} & & \text{Oxalic Acid.} \\ \left.\begin{array}{r} C_2H_4 \\ H_2 \end{array}\right\} O_2 & \begin{array}{c}\cdots\\ \cdots\end{array} & \left.\begin{array}{r} C_2H_2O \\ H_2 \end{array}\right\} O_2 & \begin{array}{c}\cdots\\ \cdots\end{array} & \left.\begin{array}{r} C_2O_2 \\ H_2 \end{array}\right\} O_2 \end{array}$$

These three compounds contain two extra radical hydrogen atoms, but while glycol is a neutral body, glycollic acid is a monobasic and oxalic acid a bibasic acid.

Although the constitution of lactic acid is quite analogous to that of glycollic acid, yet he still regarded it as a bibasic acid, although only a weak one, on account of the difficulty in replacing the second atom of hydrogen by a metal.‡

In the same year Kekulé published the first number of his "Lehrbuch." In this he showed how easily the constitution of lactic acid could be explained by going back from the radicals to the atoms. Although he then still generally used typical formulæ, these can without difficulty be transcribed into graphic.* He pointed out that the two typical or extra-radical hydrogen atoms differ from each other in the same way as that of alcohol differs from that of acetic acid. One of them is readily exchanged for metals like that of all monobasic acids, while the second does not do it so easily, but can, like that of the alcohols, be without difficulty replaced by an acid radical.

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* Compt. rend. XLVIII., 1092.

† Ann. Chem. Pharm. CXXII., 241.

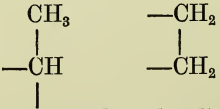
‡ Bull. Soc. Chim., 13 Mai, 1859.

Lactic acid must therefore be regarded as being at the same time an alcohol and an acid; it is derived from propionic acid $C_2H_5.CO.OH$ by substituting hydroxyl for one atom of hydrogen in ethyl, and its formula is therefore $C_2H_4(OH)CO.OH$. By the action of phosphorus chloride it yields lactyl dichloride $C_2H_4Cl.COCl$, which is identical with chloropropionyl chloride. Like other acid chlorides it is decomposed by water into hydrochloric acid and chloropropionic acid $C_2H_4Cl.CO.OH$.

The chlorine of the latter is combined with carbon in a similar way as that of ethyl chloride. On heating the latter with potash we obtain ethyl alcohol, while by the action of ammonia it is converted into ethylamine. The same two agents convert chloropropionic acid into lactic or oxyproponic acid, and into alanine or amidopropionic acid:

Chloropropionic Acid.	Lactic Acid.	Alanine.
$C_2H_4\left\{\begin{matrix}Cl\\CO.OH\end{matrix}\right.$	$C_2H_4\left\{\begin{matrix}OH\\CO.OH\end{matrix}\right.$	$C_2H_4\left\{\begin{matrix}NH_2\\CO.OH\end{matrix}\right.$

In order to get a graphic formula for lactic acid and its derivatives, it is only required to find the constitution of the group C_2H_4, which can only be expressed by one of the two following formulæ:



$$\begin{array}{c}CH_3\\|\\-CH\\|\end{array}\qquad\qquad\begin{array}{c}-CH_2\\|\\-CH_2\end{array}$$

No difficulty is encountered in deciding between these two; oxidising agents resolve lactic acid into carbon dioxide and acetic acid; but as the latter contains the group methyl CH_3, this radical must therefore also be present in lactic acid, because such a group can never be formed by oxidation. Moreover, Strecker's synthesis of alanine leads us to the same conclusion, and by modifying his method, lactic acid may be obtained more directly from aldehyde C_2H_4O, which is obtained by the oxidation of alcohol, and yields on further oxidation acetic acid; from this as well as its other chemical properties its constitution must be expressed by the graphic formula:

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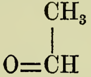
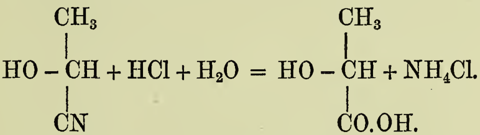
* Ladenburg, Entwichlungsgeschichte der Chemie, 274.



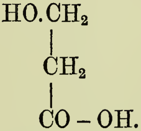
$$\begin{array}{c} CH_3 \\ | \\ O{=}CH \end{array}$$

It is oxide of ethidene, and combines with hydrocyanic acid HCN to ethidene cyanhydrate, which by the action of hydrochloric acid is converted into lactic acid and ammonia chloride:



$$\begin{array}{l} \qquad\;\; CH_3 \\ \qquad\quad | \\ HO - CH \\ \qquad\quad | \\ \qquad\;\; CN \end{array} + HCl + H_2O = \begin{array}{l} \qquad\;\; CH_3 \\ \qquad\quad | \\ HO - CH \\ \qquad\quad | \\ \qquad\;\; CO.OH. \end{array} + NH_4Cl.$$

This graphic formula of lactic acid points out the possibility of the existence of an acid having the same formula, but the following constitution:



$$\begin{array}{l} HO.CH_2 \\ \qquad\;\; | \\ \qquad CH_2 \\ \qquad\;\; | \\ \qquad CO - OH. \end{array}$$

Now such an acid is known, and, as already remarked, we find among the carbon compounds a great number of such cases, or bodies having the same percentage composition, but different chemical or physical properties.

The existence of such compounds had already been observed in the beginning of this century. Thus Dalton found, 1820, that the gas obtained by the destructive distillation of oil contained a hydrocarbon which, although combining readily with chlorine like olefiant gas, was not identical with the latter. He thought it possible that its atom (molecule) consisted of twice as much carbon and hydrogen as olefiant gas; and when his friend W. Henry, in the next year, proved the existence of such a hydrocarbon in coal gas, Dalton* stated more distinctly that the carburetted hydrogen, which he found in oil gas, was a compound *sui generis*, containing probably carbon and hydrogen in the same proportion as in olefiant gas, but its atom consisting of two of the latter.

In his classical researches on the condensation of gases, Faraday† subjected oil gas to a strong pressure, and thus obtained a liquid hydrocarbon, which is gaseous under atmospheric pressure. As Dalton had predicted, it combined with an equal volume of chlorine, but its density was twice that of olefiant gas, and its chloride contained twice as much carbon and hydrogen as Dutch liquid. Faraday expressed his opinion that we soon should become acquainted with a large number of similar bodies, having the same composition but different properties, and quotes as examples fulminic acid and cyanic acid, which as Liebig had shown, in 1825, have the same percentage composition. In spite of these observations, made by most eminent men, many chemists were of opinion that in the analysis of these bodies some mistake had been made. Berzelius could not assent to the view that compounds having an identical composition but different properties could exist. His character was quite different from that of Dalton, who did not hesitate to found the boldest speculations on the results of a few and not always very accurate experiments; while Berzelius, whose exactitude of work has hardly been surpassed, gave as his opinion that we must not jump at conclusions, and only if a large number of bodies said to have the same composition but different properties had been carefully analysed the question could be decided. For this purpose hydrocarbons were not well suited, as they did not contain the elements in very simple atomic proportions, and therefore two or more of them in some cases might, on analysis, give nearly agreeing results, without their having really the same composition. But after Wöhler had found, 1828, that ammonium cyanate readily changes into urea without alteration of weight, and Berzelius himself ascertained, 1830, that racemic acid had the same composition as tartaric acid, the latter renounced the old axiom that bodies having the same qualitative and quantitative composition must have the same physical and chemical properties. He now proposed for those which differ in their physical or chemical character the term *isomeric* (ἰσομερής, composed of equal parts), and in his annual report for 1831, he distinguished compounds which, as we now say, have different molecular weights, as *polymeric*, from those which have the same molecular weight, but contain the elements grouped together into different proximate constituents, and which he called *metameric* compounds.[*]

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* Phil. Trans. 1825, 440.

† Mem. Lit. Phil. Soc. (2) IV., 81.

A large number of such bodies are now known, and we must not forget to mention that Kolbe's prophetic eye foresaw the existence of several groups of isomerides, such as the primary, secondary and tertiary alcohols, as well as the isomeric fatty acids. On the other hand, his theory led him to the prediction of cases of isomerism, which are in opposition to the law of the linking of atoms. He was therefore opposed by the "modern chemists," as he calls those who believe in this law, and the sequence showed that he was in the wrong. Almost all cases of isomerism can now be readily explained; certain apparent exceptions have disappeared with the progress of our science, and others will undoubtedly share the same fate. We must not forget that our present theory is not a dogma, but continually changes, according to the laws of dialectic.

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[*] Pogg. Ann. XIX., 326.

The progress which has been made during the last twenty years is perhaps best seen on comparing our present views as to the causes which determine isomerism with those formerly held.

Kekulé says in his Lehrbuch, published in 1861 (I., 183), that we can divide isomeric compounds into three groups.

"We call *polymeric* those substances which contain the elements in the same proportion or have the same empirical formula but different molecular weights. To these belong among others the hydrocarbons of the series C_nH_{2n}.

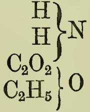
"Such bodies as are isomeric and have the same molecular weight are called *metameric*, if we understand to some extent the grouping of their atoms, or if we can express their constitution by different rational formulæ. The number is exceedingly large, as the following groups form such isomerides:

The alcohols and their ethers.
The fatty acids and their saline ethers.
The amines.
The compound ureas.
The acids of the oxalic series and their ethers, &c.

"The isomerides of these groups contain different radicals.

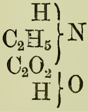
"In some cases isomeric bodies contain the same radicals, which are grouped in different ways, as for example:—

Oxamethane
(Ethyl Oxamate).



$$\left.\begin{matrix}H\\H\\C_2O_2\end{matrix}\right\}N \quad \left.\begin{matrix}C_2O_2\\C_2H_5\end{matrix}\right\}O$$

Ethyloxamic Acid.



$$\left.\begin{matrix}H\\C_2H_5\\C_2O_2\end{matrix}\right\}N \quad \left.\begin{matrix}C_2O_2\\H\end{matrix}\right\}O$$

"Besides polymeric and metameric bodies we know a number of isomeric compounds, which are not yet sufficiently studied for enabling us to express their constitution by rational formulæ. To these belong the carbohydrates of the empirical formula $C_6H_{10}O_5$, as starch, destrin, gum, and cellulose; cane-sugar and milk-sugar $C_{12}H_{22}O_{11}$, &c. These may be called isomeric *in the limited sense* (im engeren Sinn). The great number of essential oils which, like turpentine oil, have the formula $C_{10}H_{16}$, have also been classed in this group. Further, we must include in it several compounds which have the same typical formulæ, as

$$\left.\begin{array}{l}\text{Maleic acid}\\ \text{Fumaric acid}\end{array}\right\}\cdots\cdots\ \left.\begin{array}{r}C_4H_2O_2\\ H_2\end{array}\right\}O_2$$

$$\left.\begin{array}{l}\text{Mucic acid}\\ \text{Saccharic acid}\end{array}\right\}\cdots\cdots\ \left.\begin{array}{r}C_6H_8O_6\\ H_2\end{array}\right\}O_2$$

$$\left.\begin{array}{l}\text{Salicylic acid}\\ \text{Oxybenzoic acid}\end{array}\right\}\cdots\ \left.\begin{array}{r}C_7H_4O\\ H_2\end{array}\right\}O_2$$

"These formulæ cannot be called rational, as we knew neither the nature nor the constitution of their radicals; they only show that they are bibasic acids.

"One of the most remarkable examples of isomerism, which we cannot yet explain, is found in the dichlorides of ethylene and ethylidene $C_2H_4Cl_2$; the former being formed by the direct combination of ethylene and chlorine as well as by action of phosphorus pentachloride on glycol, while the same reagent converts aldehyde into ethylidene dichloride." Citing other cases, Kekulé says, "it is obvious that by a more complete study of such bodies it will be found that they are either polymeric or metameric, and in the latter case their isomerism will be found to be caused a difference in the relative position of their atoms.

"Finally, we have a class of isomeric bodies, which, although having essentially the same chemical properties, exhibit different physical properties, such as the two modifications of tartaric acid and other physical isomerides, one of which turns the plane of polarised light to the right and the other to the left."

CHAPTER VIII.

ISOMERIC PARAFFINS.—PRIMARY, SECONDARY, AND TERTIARY ALCOHOLS.—METAMERIC ETHERS.- NON-SATURATED COMPOUNDS.

Let us now compare the views held about 20 years ago, with those to which the law of the linking of atoms has led us, beginning with the most simple hydrocarbons—the paraffins.

The lowest member, marsh gas or methane, exists only in one form, and we cannot imagine that such a simple body could exist in two or more isomeric modifications. But its next homologue C_2H_6 was formerly believed to exist in two isomeric forms. One of these had been obtained by Kolbe as a product of electrolytic decomposition of acetic acid, while Frankland prepared it by heating methyl iodide with zinc; this was called methyl, or afterwards dimethyl. The second was also discovered by Frankland, who prepared it by heating ethyl iodide with zinc and water under pressure, and called it ethyl hydride. The following formulæ were given to these hydrocarbons:

$$\begin{array}{cc} \text{Dimethyl.} & \text{Ethyl Hydride.} \\ \left.\begin{array}{c} CH_3 \\ CH_3 \end{array}\right\} & \left.\begin{array}{r} C_2H_5 \\ H \end{array}\right\} \end{array}$$

Kekulé describes these and other supposed isomeric hydrocarbons of this group without endeavouring to explain the cause of their isomerism. To do that it was afterwards assumed that the four combining units of the carbon atom had not the same value or function. But Crum-Brown* showed that there is a certain degree of inconsistency in this hypothesis. Butlerow, in endeavouring to explain the isomerism of methyl gas and ethyl hydride, argued that in the former the two atoms of carbon were united by two combining units of the same kind which he called secondary affinities, each being the combining unit which in methyl iodide is saturated with iodine. In hydride of ethyl the carbon atoms are united in the same way as in other ethyl compounds, and therefore probably as in the acetyl compounds, one of which is methyl cyanide or acetonitril; the one is therefore the combining unit of methyl, and the other that of cyanogen. These must be different, because the two hydrocarbons are not identical. To indicate this, Butlerow calls the free combining unit of cyanogen a primary affinity. We have thus in methyl two secondary affinities united together, and in hydride of ethyl a primary united to a secondary. "But by carrying this argument a little further, we arrive," says Crum-Brown, "at an absurdity; thus the carbon radical of acetic acid is the same as that of oxyacetic acid, and that again is the same as that of the carbon radical of oxalic acid, and therefore as that of oxalic nitril or cyanogen gas. In cyanogen gas, however, we have the two carbon atoms united by two primary affinities; but we have before proved that in the acetic acid series they are united by a primary affinity of the one to a secondary of the other. It is obvious, then, that at least one of our assumptions is false."

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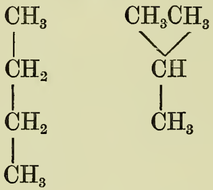
* Trans. Roy. Soc. Edin., XXIII., 707.

About the same time the author proved by experiment that methyl gas or dimethyl is identical with ethyl hydride,* and since that time other proofs have been found showing that the four combining units of the carbon atom have the same value.

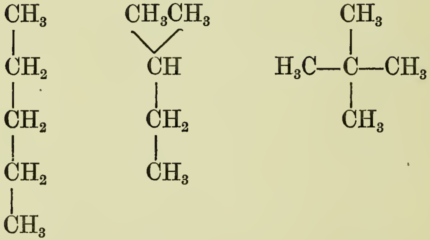
Now, if such be the case, the law of the linking of atoms points out that the next homologue C_3H_8 cannot exist in isomeric forms, but the following member in two and the next in three:

C_4H_{10}



Boiling point +1° —17°

C_5H_{12}



Boiling point 38° 30° 9·5°

This theory is completely borne out by facts; we are acquainted with these hydrocarbons. If we ascend in the series we find that the number of possible isomerides rapidly increases. Professor Cayley† has calculated that up to the hydrocarbon $C_{13}H_{28}$ theory predicts the following:—

C=	1	2	3	4	5	6	7	8	9	10	11	12	13
Number of paraffins.	1	1	1	2	3	5	9	18	35	75	159	357	799

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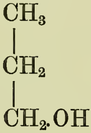
* Proc. Roy. Soc. XIII., 225; Journ. Chem. Soc., N. S. II., 263.
† Brit. Ass. Report, 1876, 257.

Of these comparatively few are known; whether all these can exist, and if so, whether we can distinguish them from each other, is a question which time only will solve.

If we replace in a paraffin one atom of hydrogen by other elements or radicals, we obtain compounds of monad radicals, which have been called the alcohol radicals, because the alcohols are those of their derivatives which have been known longest, and generally yet serve as the starting point for the preparation of other compounds.

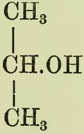
Theory predicts that the number of alcohols is larger than that of the paraffins, and as far as our experience goes is in perfect accordance with facts.* Thus only one methyl alcohol $CH_3.OH$ and one ethyl alcohol $C_2H_5.OH$ can exist, but we know 2 propyl alcohols $C_3H_7.OH$ and 4 butyl alcohols $C_4H_9.OH$, viz.:

Primary Propyl Alcohol.



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array}$$

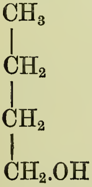
Secondary Propyl Alcohol or Dimethyl Carbinol.



$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_3 \end{array}$$

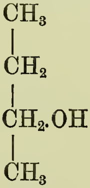
Boiling point... 97° 84°

Primary Normal Butyl Alcohol.



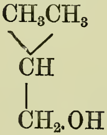
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2.OH \end{array}$$

Secondary Butyl Alcohol or Methyl-ethyl Carbinol.

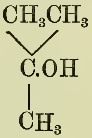


$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2.OH \\ | \\ CH_3 \end{array}$$

Isobutyl Alcohol.



Tertiary Butyl Alcohol.



B. pt. 117° 97° 109° 82·5°

Now the question arises, how can we elucidate the constitution of these isomerides? The method is exactly the same as that by which the constitution of acetic acid, lactic acid, &c., has been made out, the principle being either to build up the molecule from smaller ones or to resolve it into such.

One of the propyl alcohols has been first found by Chancel in the fusel oil of spirits of wine, obtained by the fermentation of the marc of grapes. In its chemical character it exhibits the closest analogy to ethyl alcohol, and yields on oxidation first propionaldehyde C_3H_6O, and then propionic acid $C_3H_6O_2$. The latter is obtained synthetically from ethyl alcohol, by converting it into the cyanide or propionitril $C_2H_5.CN$, which, on heating with an aqueous alkali, is converted into propionic acid $C_2H_5.CO_2H$. This acid can again be reduced to the corresponding alcohol by a reaction which is a general and important one, and of which more will be said hereafter. On heating a mixture of calcium propionate and calcium formiate, propionaldehyde and carbon dioxide are produced:

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* The number of isomeric alcohols containing x atoms of carbon is equal to that of the isomeric paraffins containing $x+1$ carbon atoms.

$$(C_2H_5.CO_2)_2Ca + (HCO_2)_2Ca = 2C_2H_5.COH + 2CaCO_3.$$

Propionaldehyde combines with hydrogen in the nascent state, the alcohol being formed.

All these reactions point clearly out that the constitution of this body is expressed by the first of the above graphic formulæ.

The second propyl alcohol was discovered by Friedel, who obtained it by combining acetone C_3H_6O with hydrogen. Acetone is a volatile liquid, obtained by the dry distillation of the acetates of calcium, lead, and other metals, and was already known to the older chemists. Thus Libavius says in his "Alchemia" that by strong heat the quintessence could be expelled from sugar of lead.

Acetone has also been obtained synthetically by Freund by acting with zinc-methyl on acetyl chloride:

$$CH_3.COCl + Zn(CH_3)_2 = CH_3.CO.CH_3 + Zn(CH_3)Cl$$

The secondary propyl alcohol formed by combining acetone or dimethyl ketone with hydrogen yields on oxidation again the latter compound, which by further oxidation is resolved into acetic and formic acids.

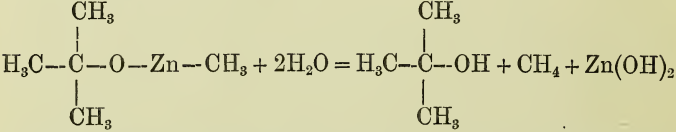
Of the four butyl alcohols, one was discovered in the fusel oil of the marc of grapes, by Wurtz, who found it to possess the characteristic properties of common alcohol; like the latter, it yielded on oxidation an aldehyde and an acid which was believed to be identical with butyric acid $C_4H_8O_2$, which occurs in butter and is obtained artificially from sugar by butyric fermentation. At that time there was not the least suspicion of the existence of isomeric alcohols, and the butyl alcohol was regarded as a true homologue of spirits of wine. Still there was one point which yet puzzled chemists for a long time. Hermann Kopp had by a series of most careful investigations established the law that in homologous series the boiling point increases regularly for each increase of CH_2, the increment in the series of alcohols being about 19°. Now as ethyl alcohol boils at 78·4° and propyl alcohol at 97°, the boiling point of the next homologue ought to be 116° instead of 109°.

This discrepancy was afterwards cleared up by Erlenmeyer and Markownikoff. It was found that the butyric acid formed by the oxidation of the alcohol is not identical with that found in butter and obtained from sugar, not only their salts exhibiting characteristic differences, but also their boiling points, that of the former being 154° and of the latter 162°. The lower boiling compound, which we now call isobutyric acid, is produced synthetically from secondary propyl iodide in the same way as acetic acid from methyl iodide; on replacing in the former the iodine by cyanogen we obtain isobutyronitril, which, on boiling with a solution of potash, is converted into isobutyric acid, from which it follows that the chemical structure of the alcohol is expressed by the second formula.

A fresh proof was found by Frankland and Duppa, who obtained isobutyric acid by replacing two atoms of hydrogen in acetic acid by methyl, while by substituting ethyl for one atom, common butyric acid was formed, showing that it corresponds to the primary normal butyl alcohol, which afterwards was obtained from this acid by Lieben and Rossi in the same way as they prepared the normal propyl alcohol from propionic acid.

A third butyl alcohol was obtained by de Luynes from erythrite $C_4H_6(OH)_4$, a body nearly allied to mannite and sugar. Although this reaction did not indicate its chemical structure, no doubt could be entertained about it; it bears the greatest analogy to secondary propyl alcohol, yielding on oxidation first methyl-ethyl ketone $CH_3.CO.C_2H_5$, which is also formed by the action of zinc ethyl on acetyl chloride, and is resolved by oxidation into two molecules of acetic acid. De Luynes' alcohol is therefore represented by the third graphic formula.

The fourth butyl alcohol was discovered by Butlerow, who, by acting on acetyl chloride with an excess of zinc methyl, obtained a white crystalline mass, which by the action of water is resolved into a butyl alcohol, marsh gas, and zinc hydroxide. This reaction does not clearly indicate the chemical structure of the new alcohol, but we can explain it most simply by the following hypothesis:—When we act on acetyl chloride with zinc methyl we obtain acetone, which, as we have seen, combines with hydrogen in the nascent state and is converted into secondary propyl alcohol. In a similar way it may combine with zinc methyl to form the crystalline compound already mentioned, which, by the action of water, yields tertiary butyl alcohol:



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-O-Zn-CH_3 + 2H_2O = H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH + CH_4 + Zn(OH)_2$$

That the alcohol has this constitution has since been proved in other ways, of which more hereafter. On oxidation it is resolved into acetic acid and formic acid, which latter in the nascent state is generally further oxidised to carbon dioxide or water.

The above examples have been chosen for illustrating the methods now in use for finding out the constitution of isomeric alcohols. The alcohols are divided into three groups: *primary*, *secondary*, *tertiary*; and if we only want to know to which of these an alcohol belongs, we merely study its products of oxidation:

(1) A primary alcohol yields in this case first an *aldehyde*, which is readily further oxidised to a fatty acid, containing the *same number of carbon atoms in the molecule as the alcohol.*

(2) A secondary alcohol is by oxidation first converted into a *ketone*, which is less oxidisable than an aldehyde; but if oxidised, its molecule breaks up into *two fragments* according to a law established by Popoff, which says, that one alcohol radical remains in combination with carbonyl CO, yielding a fatty acid, while the second alcohol radical is oxidised in exactly the same way as the corresponding alcohol would be.

(3) A tertiary alcohol yields neither an aldehyde nor a ketone, but is, as Butlerow has shown, broken up into *three fragments*; one of the alcohol radicals remaining combined with the carbon atom which keeps the molecule together, while the two others yield the same oxidation products as their corresponding alcohols.

In examining the constitution of such compounds great aid is often given by studying their physical properties, such as the boiling points. Thus a normal compound, by which we mean one in which the carbon atoms form a single chain, boils always higher than any of its isomerides, the boiling point of the latter being higher the more simple their constitution is. Further, a primary alcohol boils at a higher temperature than a secondary, and this again higher than an isomeric tertiary, &c., as the examples given clearly show.

Metameric with the alcohols are the ethers, which can easily be distinguished from them not only by chemical reactions but also by their boiling points, which are always much lower than those of the alcohols; thus we know the two following metamerides of the butyl alcohols :

	Diethyl Ether.	Methylpropyl Ether.
	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$	$\left.\begin{matrix}CH_3\\C_3H_7\end{matrix}\right\}O$
Boiling point	35·5°	50°

Naumann has shown that in such cases the boiling point is the lower the nearer the oxygen is placed to the centre of the chain of atoms :—

Normal Butyl Alcohols.

		Boiling Point.
Primary......	$CH_3.CH_2.CH_2.CH_2.OH$	116°
Secondary ...	$CH_3.CH_2.CH(OH).CH_3$	97°

Normal Ethers.

Methyl propyl...	$CH_3.CH_2.CH_2.O.CH_3$	50°
Diethyl	$CH_3.CH_2.O.CH_2.CH_3$	35·5°

The paraffins and their substitution products have been called *saturated* compounds because we cannot combine them with other molecules, as is the case with the so-called *non-saturated* compounds, which are derived from the former by the abstraction of hydrogen.

Thus, if we remove two atoms of this element from the paraffins, we obtain the homologous series of the olefines, which in their physical properties, as specific gravity, boiling points, &c., exhibit great resemblance to the corresponding members of the paraffin group. They are, however, easily distinguished from the latter by combining directly with one molecule of the elements of the chlorine group or their hydracids.

To account for their constitution three hypotheses have been enunciated :—

(1) They contain carbon atoms with free combining units.

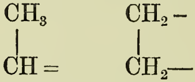
(2) One of the carbon atoms is no longer a tetrad, but a dyad.

(3) One carbon atom is linked with two combining units to two combining units of another.

The first hypothesis found many adherents several years ago. Amongst these Lothar Meyer* has very clearly stated the reasons why the hypothesis that the so-called non-saturated compounds contained free-combining units was much more probable than Kekulé's view, that a double linking of carbon atoms occurred in them. He says: "In the first place, this hypothesis offers no philosophical difficulty; it cannot be astonishing that, under certain conditions, one or more affinities remain unsaturated; on the contrary, it would be wonderful if free affinities did not exist."

"For certain compounds this theory is even unavoidable, as for nitric oxide, carbonic oxide, the vapours of mercury, cadmium, &c."

Now according to this theory the most simple olefine known, ethene C_2H_4, ought to exist in two isomeric modifications:



$$\begin{array}{c} CH_3 \\ | \\ CH= \end{array} \qquad \begin{array}{c} CH_2- \\ | \\ CH_2- \end{array}$$

However, experiments made by Meyer and Tollens, for the purpose of obtaining an isomeride of ethene, failed. But although the two isomeric forms of ethene had not been obtained, yet it was stated that two different chlorine substitution products of ethene existed, *i.e.*, *monochlorethene* or *vinyl chloride* C_2H_3Cl, which Regnault obtained by heating ethene dichloride with potash, and *chloracetene*, which Harnitz-Harnitzky prepared by the action of phosgene $COCl_2$ on aldehyde. As both compounds had been repeatedly investigated by other chemists, their existence could hardly be doubted, and only be explained by assuming either free combining units or the theory of dyad carbon.

The existence of two isomerides C_2H_3Cl was, theoretically, of the highest importance, because, as Kekulé pointed out, if carbon really can exist as a dyad in such a simple case, the same assumption is at least admissible in more complicated ones. Kekulé and Zincke† therefore repeated Harnitzky's experiments. They said that from their theoretical standpoint the existence of chloracetene not only appeared improbable, but that the properties ascribed to this body, as well as the reaction by which it was formed, were so remarkable that it appeared necessary to make the personal acquaintance of this body. Although it appeared improbable that this compound was really isomeric with Regnault's vinyl chloride, yet it might be a polymeride, which by dissociation yielded a lighter vapour. It was also possible that vinyl chloride had not been obtained in a pure state, and was identical with chloracetene, and there was also the probability that all the statements about the latter compound were erroneous. The result was that the last view was correct. Kekulé and Zincke found "that the most remarkable property of this remarkable compound was its non-existence." It turned out to be a mixture of phosgene with a polymeric modification of aldehyde.

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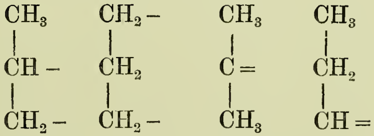
* Ann. Chem. Pharm. CXXXIX., 285.

† Ann. Chem. Pharm. CLXII. 125.

According to the theory of dyad carbon, only one ethene can exist having the constitution $\mathrm{CH_3{-}CH}$. But that the known hydrocarbon has not this structure is proved by the fact that ethene chlorhydrate $\mathrm{C_2H_4(OH)Cl}$ yields on oxidation chloracetic acid.

Another proof against the existence of free combining units or dyad carbon is found in the fact that only one propene, $\mathrm{C_3H_6}$, is known, of which hydrocarbon four modifications ought to exist according to the first theory, viz.:



$$\begin{array}{cccc} \mathrm{CH_3} & \mathrm{CH_2-} & \mathrm{CH_3} & \mathrm{CH_3} \\ | & | & | & | \\ \mathrm{CH-} & \mathrm{CH_2} & \mathrm{C=} & \mathrm{CH_2} \\ | & | & | & | \\ \mathrm{CH_2-} & \mathrm{CH_2-} & \mathrm{CH_3} & \mathrm{CH=} \end{array}$$

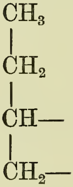
or only the latter two in the case of the dyad carbon theory. We know, however, the four corresponding dichlorides and dibromides; but if we heat these with sodium to remove the chlorine or bromine they all yield one and the same hydrocarbon, which is also obtained by abstracting the elements of hydriodic acid from the primary or secondary propyl iodide, and which on combining again with this acid is converted into the secondary iodide. From these reactions it follows that if we still assume the existence of free combining units, the constitution of the hydrocarbon is expressed by the first of the above formulæ.

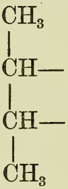
While we know only one ethene and one propene, we are acquainted with three butenes $\mathrm{C_4H_8}$, which have been predicted by

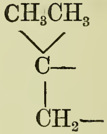
Kekulé's theory, that in the olefines two carbon atoms are linked together by two of the combining units of each; according to the other hypotheses more ought to exist. These three are readily obtained by heating the four butyl iodides with alcoholic potash, which removes the elements of hydriodic acid:

$$C_4H_9I + KOH = C_4H_8 + KI + H_2O.$$

The normal iodine yields an olefine which is isomeric with that from the secondary compound, but both on being combined again with hydriodic acid are converted into secondary butyl iodine. The third isomeride is produced by the above reaction from either isobutyl iodide or the tertiary iodide, and is again converted into the latter by combining it with hydriodic acid. Now, again assuming that these olefines contain free-combining units, their constitution could only be expressed by the following graphical formulæ:—







In other words, it has been proved in these cases and all others, that the carbon atoms which are not saturated with hydrogen are always two adjoining ones. The most simple and therefore the most probable hypothesis is, that these two atoms are joined together by a double linking, which however readily changes again into the single linking.

By again abstracting hydrogen from the olefines we obtain the hydrocarbons of the series C_nH_{2n-2}, which may be converted into those of the group C_nH_{2n-4}, &c. All such hydrocarbons or their substitution products, amongst which, of course, many cases of isomerism occur, have the tendency to combine directly with the members of the chlorine group, the hydracids and other molecules to form *additive* compounds, in which the carbon atoms are linked together in the most simple way possible. Thus *dipropinyl* C_6H_6 easily combines with bromine to form the octobromide $C_6H_6Br_8$ or hexane, in which 8 atoms of hydrogen are replaced by bromine.

CHAPTER IX.

THE AROMATIC GROUP.—KELULÉ'S HYPOTHESIS.—THE DISUBSTITUTION PRODUCTS OF BENZENE, PARA-COMPOUNDS, ORTHO-COMPOUNDS, META-COMPOUNDS.—THE POSITION OF ATOMS IN SPACE.

Isomeric with dipropinyl is *benzol* or *benzene*, which however possesses quite a different chemical character; it is the most simple compound of a large group of bodies, which Kekulé has called the *aromatic compounds*, because many of them are found in essential oils, balsams, gum-resins, and other bodies having an aromatic smell, while the bodies described above belong to the *fatty compounds*, so called because the homologous series of the fatty acids is that which was first most completely known.*

Benzene may be called the marsh gas of the aromatic group, inasmuch as all other compounds belonging to it must be considered as substitution products of benzene or derived from it by replacing hydrogen by other elements or radicals. The aromatic compounds have been very fully investigated during the last 25 years. We owe our present theory of their constitution to Kekulé, who had to account for the following points:

(1) Benzene and other aromatic hydrocarbons resemble the paraffins in so far that they readily form substitution products.

(2) Under certain conditions they can also form additive compounds, but not more than six monads at the highest can thus be added; thus benzene can yield a hexbromide $C_6H_6Br_6$, but not an octobromide, like the isomeric dipropinyl.

(3) Among the monosubstitution products of benzene no isomerides are known.

(4) The disubstitution products of this hydrocarbon exist in three isomeric forms.

Now as no isomeric monosubstitution products exist, it follows that each carbon atom must be combined with another in exactly the same way, and each also be combined with one atom of hydrogen. These conditions are fulfilled by assuming the carbon atoms forming a closed chain or ring, being linked together by one and two combining units alternately, the graphic formula of benzene being :

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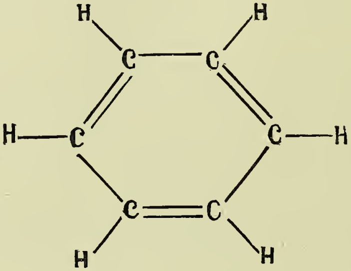
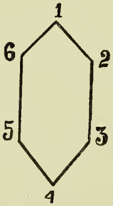
* Kekulé understands by fatty bodies only the so-called saturated compounds, while to those containing less hydrogen, but which strictly speaking are, as we have seen, also saturated, he gives the name "Wassertsoffärmere Verbindungen" (compounds poorer in hydrogen), and to distinguish them from the aromatic bodies, he calls the latter "Kohlenstoffreichere Verbindungen" (compounds richer in carbon).



That a body of such a symmetrical structure forms more readily substitution products than additive compounds is not difficult to understand, and it is also easy to see why benzene may combine directly with one, two, or three molecules of chlorine or bromine, but not with more.

The existence of three isomeric disubstitution products is also readily explained. If we represent benzene as a hexagon and number the six corners where the carbon atoms are supposed to be, thus :



we find that two atoms of hydrogen may be replaced at 1 and 2 ; 1 and 3 ; 1 and 4 ; no other cases being possible, as 1, 5 = 1, 3 ; 1, 6 = 1, 2, &c.

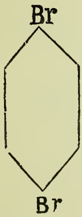
Moreover, we are not only able to explain on this theory the cause of this isomerism, but we can also determine the relative positions of the replaced hydrogen atoms.

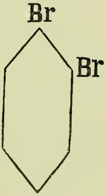
The first attempts made in this direction failed, partially, because the number of facts then known were not sufficient to build up a satisfactory hypothesis ; and also because it was assumed that, if we exchange atoms or radicals by double decomposition, those entering the molecule would occupy the place of those which have been removed. This however is not always the case; it often happens that in such reactions a shifting of atoms, or intramolecular change takes place, by which the relative positions of the atoms are completely altered.

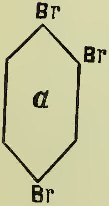
It was therefore first required to find out under what conditions this may happen, and to eliminate those reactions which are liable to produce such a result.

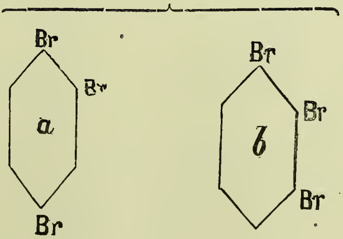
Of the different methods which have been used to elucidate the constitution of the disubstitution products of benzene those employed by Griess and by Körner are the most important. We will first shortly describe that of the latter chemist, as it is the most simple.* He starts from the three dibromobenzenes:

These by further substitution can give rise to the formation of *only three* tribromobenzenes, but the first or *paradibromobenzene* can yield only *one*, the second or *orthodibromobenzene* can furnish *two* of them, while all *three* may be obtained from the last or *metadibromobenzene*, as the following diagrams will show, in which we distinguish the tribromobenzenes by *a*, *b* and *c*.









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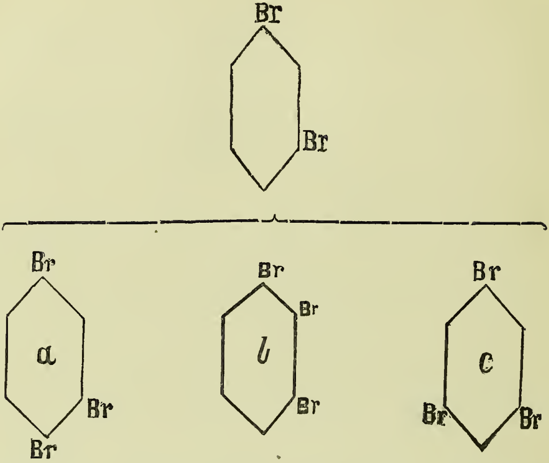
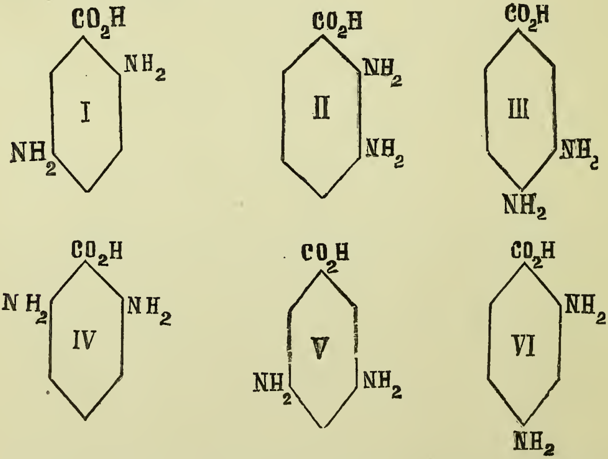
* Gazetta Chimica Italiana, IV., 305; abstracted in Journ. Chem. Soc., 1876, I., 204.



Griess* in his demonstration took the opposite way; he showed that *six diamidobenzoic acids* $C_6H_3(NH_2)_2CO_2H$ can exist, which, by taking away the group CO_2, will furnish only *three diamidobenzenes.* The constitution of these acids is expressed by the following graphic formulæ:—



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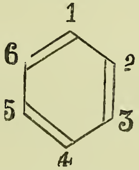
[*] Ber. deut. Chem. Ges. VII., 1226, and Journ. Chem. Soc., 1875, 263.

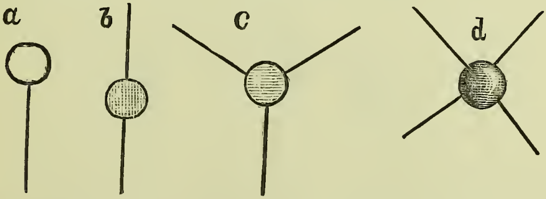
I. yields *paradiamidobenzene,* II. and III. both give rise to formation of *orthodiamidobenzene,* while *metadiamidobenzene* can be obtained from IV., V., and VI.

We know the constitution of the three dibromobenzenes and the three diamidobenzenes, which can be easily distinguished by their physical properties, such as melting point or boiling point; now these bodies can, by simple reactions, be obtained from or converted into a large number of other disubstitution products, and thus the constitution of almost all of them is known.

Kekulé's formula explains not only the constitution of these, but also of many more complicated aromatic compounds in a very clear way. But one objection has been raised against it by Ladenburg who has pointed out that the positions 1, 2 and 1, 6 were not identical, as the following diagram will illustrate:

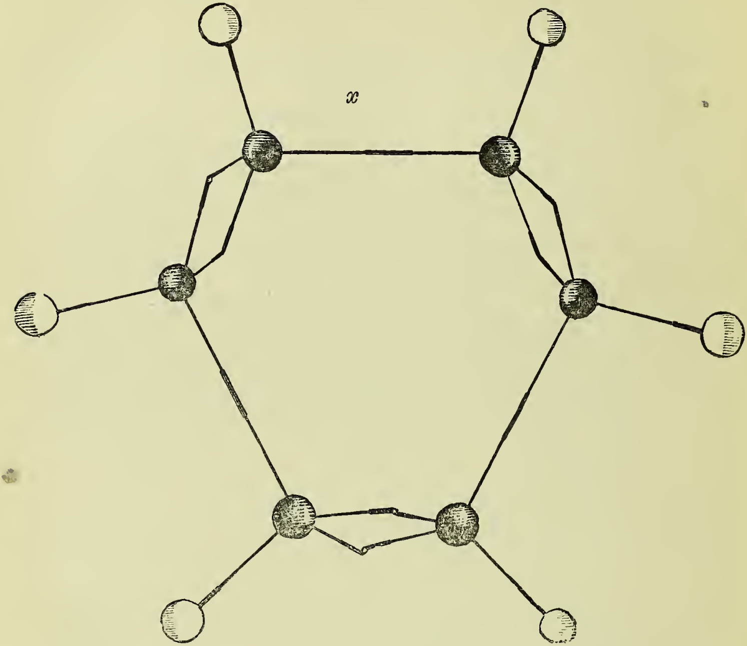


consequently four distribution products ought to exist instead of three, which however is not the case. Other formulæ have therefore been proposed; of these we will represent Ladenburg's and Körner's, together with that of Kekulé, by drawings made from photographs of Kekulé's glyptic models.

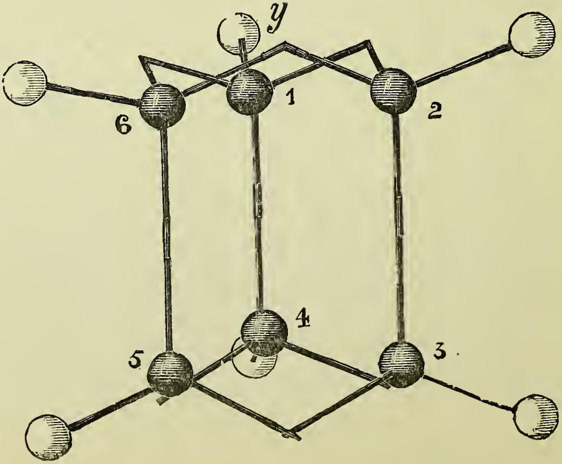


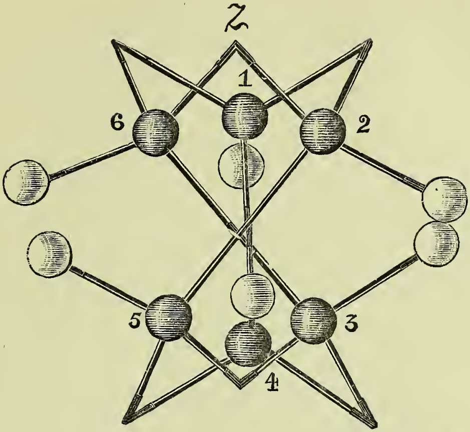
These models consist of wooden balls of different colour and provided with brass rods, by which any number may be joined together by links or hasps. The white ball *a* represents monad hydrogen, and the red ball *b* dyad oxygen; *c* is a blue ball with three combining units, representing nitrogen or any other triad element, while the black ball *d* is meant for tetrad carbon.

Kekulé's glyptic formula of benzene is shown in fig. *x* :


x

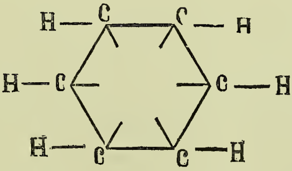
whilst fig. *y* shows that which Ladenburg has proposed, and fig. *z* that of Körner.


y



It is not our intention to discuss the meaning of these glyptic formulæ more minutely. It will be sufficient to say that in the two latter, the position 1, 2 represents the meta-compounds and 1, 3 the ortho-compounds, which is not difficult to make out.

Objections to these formulæ have also been made; of these we may mention that of van't Hoff* and of Lothar Meyer.† The latter thinks that all difficulties would disappear by assuming benzene to contain six free combining units, its graphical formula being expressed as follows:



Kekulé,‡ however, has shown that his view is more in accordance with observed facts than any other which has been proposed. He says that the apparent difference between the positions 1, 2 and 1, 6 takes its origin rather from the model employed than from the ideas, of which this model affords only an imperfect representation. To show that no such difference exists he brings forward the following hypothesis.

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* Ber. deutsch. Chem. Ges., IX., 1882.

† Moderne Theorien.

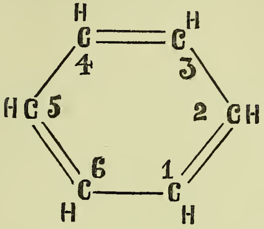
‡ Ann. Chem. Pharm., CLXII., 77; Jour. Chem. Soc., 1872, 612.

The atoms in the systems which we call molecules must be considered to be continually in motion, but hitherto no explanation as to the nature of this intramolecular motion has been given, which of course must be in accordance with the law of the linking of the atoms. A planetary motion seems, therefore, not admissible, the movement must be of such a kind that all the atoms forming the system retain the same relative arrangement, in other words, that they return to a mean position of equilibrium. The most probable assumption, and which is in accordance with the view held by physicists is, that the motion of the atoms takes place in what may be considered a straight line, and that on striking each other, they recoil like elastic bodies. What we call valency would then be nothing but the number of contacts experienced by one atom on the part of other atoms in the unit of time. In the same time that the monad atoms of a diatomic molecule like H_2 strike each other once, the dyad atoms of a diatomic molecule come in contact with each other twice, the temperature in both cases being the same. In a molecule consisting of one dyad and two monads as H_2O, the number of contacts in the unit of time is $= 2$ for the former and $= 1$ for each of the latter.

If two atoms of carbon are linked together by one combining unit of each, they strike against each other once in the unit of time, or in the same time in which monad hydrogen makes a complete vibration; during this same time they encounter three other atoms. Carbon atoms linked together by two bonds of each come into contact twice in the unit of time, and encounter during the same time two other atoms.

If we now apply these views to benzene, we come to the following view. Each carbon atom strikes against two others in the unit of time, once against the one and twice against the other. In the same unit of time it comes once in contact with the hydrogen atom, which during the same period makes a complete vibration.

Accordingly in the graphic formula :



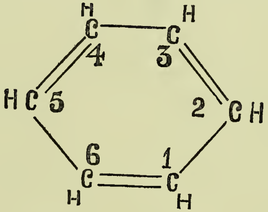
the contacts of the atom 1 in the unit of time may be thus represented, if *h* stands for hydrogen :

1 : 2, 6, *h*, 2.

In the second unit of time they are

2 : 6, 2, *h*, 6,

which would be represented by the following formula :



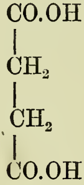
The same carbon-atom is therefore, during the first unit of time, linked to one of the adjoining ones by one, and during the second unit of time by two of its combining units ; and *vice versa* with regard to the other adjoining carbon atom.

The variation of these contacts undergone by a carbon-atom exhausts itself in these two units of time ; its sum, viz.,

2, 6, *h*, 2, 6, 2, *h*, 6

represents the whole series of possible contacts under these circumstances, and therefore repeats itself continually. From this it is evident that carbon atom strikes against the two others, with which it is directly combined, an equal number of times, *i.e.*, that it bears the same relation to both. The ordinary graphic formula only represents the contacts made during the first unit of time, and thus the view has sprung up that in the distribution products the positions 1, 2 and 1, 6 must produce different compounds. If the above or some similar conception be correct, it follows that no real difference exists.

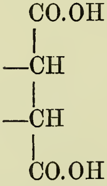
It has already been stated that there exist some cases of isomerism which the theory of the linking of atoms is not capable of explaining. Of these we will take one case; we know two acids called *fumaric acid* and *maleic acid*, $C_4H_4O_4$, which are readily transformed one into the other, and which combine with hydrogen to form succinic acid $C_4H_6O_4$. The constitution of the latter is exactly known, and is expressed graphically thus :—



$$\begin{array}{l} CO.OH \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

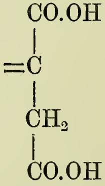
But how can such a compound by the loss of two atoms of hydrogen yield two isomeric acids? The only plausible explanation which could be given was, that they contained free combining units, as for instance :

Fumaric Acid,



$$\begin{array}{l} CO.OH \\ | \\ -CH \\ | \\ -CH \\ | \\ CO.OH \end{array}$$

Maleic Acid.



$$\begin{array}{l} CO.OH \\ | \\ =C \\ | \\ CH_2 \\ | \\ CO.OH \end{array}$$

We have, however, seen that the existence of free combining units in such compounds is very improbable. On the other hand, our graphic formulæ represent the position of the atoms only in a plane, while of course they are really placed in space of three dimensions starting with this argument, van't Hoff* has lately brought forward a hypothesis for explaining this and similar cases of isomerism. According to it we may represent a carbon atom as a tetrahedron, its four combining units being represented by the corners, and obtain thus the following glyptic formula of succinic acid :

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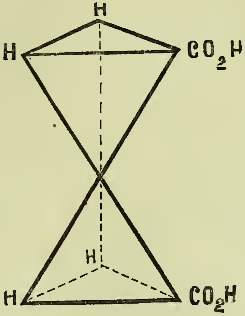
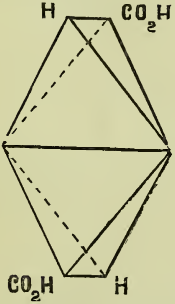
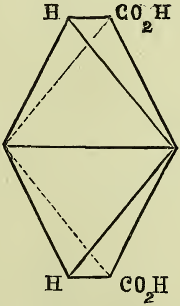
* La chimie dans l'espace; published in German by Herrmann as: Die Lagerung der Atome im Raume.



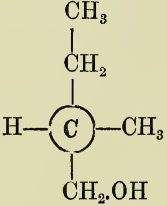
An isomeric modification of such a compound cannot exist, because if we arrange the hydrogen atoms or the carboxyls which are combined with the same carbon-atom, differently, we can, by turning one of the tetrahedrons round, always obtain the above figure. But if we take two atoms of hydrogen away, two different compounds may be formed, in which the atoms are arranged as follows :


Fumaric Acid.


Maleic Acid.

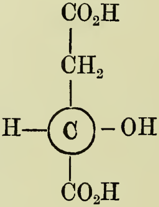
In a similar way van't Hoff tries to explain certain cases of *physical* isomerism as that of compounds having the same chemical properties but acting differently on polarised light, some of them turning its plane to the right, others to the left. We cannot however discuss the subject any further, and may only add that Le Bel and van't Hoff have found that all optically active compounds contain one or more *asymmetric* carbon-atoms, *i.e.*, such as are combined with 4 different atoms or groups, as the following examples will show, in which these atoms are clearly marked :—

Active Amyl Alcohol.



$$\begin{array}{ccc} & CH_3 & \\ & | & \\ & CH_2 & \\ & | & \\ H- & \textcircled{C} & -CH_3 \\ & | & \\ & CH_2.OH & \end{array}$$

Malic Acid.



$$\begin{array}{ccc} & CO_2H & \\ & | & \\ & CH_2 & \\ & | & \\ H- & \textcircled{C} & -OH \\ & | & \\ & CO_2H & \end{array}$$

CHAPTER X.

The Synthesis of Organic Bodies.—Urea.—Acetic Acid.—The Paraffins.—Acetylene.—The Fats.—Vegetable Acids.

It has already been stated that as soon as a clear insight into the constitution of organic bodies was gained, methods were found by means of which bodies hitherto formed only by the vital process could be built up from their elements. The first compound thus obtained (see p. 17) is urea, which Wöhler, in 1828, prepared artificially. No further progress in organic synthesis was made up to 1845, when a method of obtaining acetic acid from the elements was discovered. Kolbe found that by the action of chlorine on carbon disulphide CS_2, a body readily obtained by the direct combination of its elements, the sulphur is replaced by chlorine, and carbon tetrachloride or tetrachlormethane CCl_4 is formed, which, when passed through a red-hot tube, yields free chlorine and tetrachlorethene C_2Cl_4. By acting on this compound with chlorine in the presence of water, trichloracetic acid is formed, the reaction taking place in two stages :

$$(1) \quad C_2Cl_4 + Cl_2 = C_2Cl_6.$$

$$(2) \quad C_2Cl_6 + 2H_2O = C_2Cl_3HO_2 + 3HCl.$$

In the same year Melsens found that by subjecting trichloracetic acid to the action of hydrogen in the nascent state, the latter replaces the chlorine, acetic acid being formed. In the next year he succeeded by the same inverse substitution in converting carbon tetrachloride CCl_4 into marsh gas CH_4, which up to 1848 was the only member of the paraffin group known to chemists. Since that year the researches of Kolbe* on the electrolysis of the fatty acids, and those of Frankland on the action of zinc on the iodides of the alcohol radicals,† opened a new field of discovery, from which in rapid succession rich harvests have been reaped. The hydrocarbons thus isolated were considered by their discoverers to be the free radicals of the alcohols, and in consequence the molecular weights then given to these bodies were only one half of those now accepted.

In their report to the French Academy upon these hydrocarbons, Laurent and Gerhardt proposed that their formulæ should be doubled, in accordance with Avogadro's law. They regarded them as true homologues of marsh gas, which view was also pronounced by Hofmann, who pointed out that, if the formulæ of Kolbe and Frankland were accepted, the increment of the boiling point produced by an increase of CH_2, would be twice that, which it ought to be according to Kopp's law.

Besides these radicals, Frankland discovered another series of hydrocarbons which, in accordance with their mode of formation, he regarded as the hydrides of alcohol radicals and the true homologues of marsh gas, and which, as Brodie first pointed out, stood in a similar relation to the radical hydrocarbons as the alcohols stand to their ethers:

$$\begin{array}{cc} \text{Ethyl Hydride.} & \text{Ethyl.} \\ \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\} & \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\} \\ \text{Ethyl Alcohol.} & \text{Ethyl Ether.} \\ \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O & \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O \end{array}$$

Brodie also anticipated the existence of mixed radicals, bearing the same relation to the simple radicals as Williamson's mixed ethers to common ether:

$$\begin{array}{cc} \text{Methyl-ethyl.} & \text{Methyl-ethyl Ether.} \\ \left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\} & \left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O \end{array}$$

The researches of Wurtz soon fully realised this anticipation; he found that, by the action of sodium on the iodides, the alcohol radicals were easily obtained, and by employing two different iodides at the same time mixed radicals were formed. The results of Wurtz' researches were considered as a convincing proof of the correctness of Brodie's views, and it was hence generally believed that the hydrocarbons, which are now called the paraffins, formed two distinct groups, one of them called the *hydrides*, being compounds of an alcohol radical with hydrogen, while each molecule of those of the second group was made up of two radicals, just as a molecule of hydrogen consists of two atoms.

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* Ann. Chem. Pharm. LXIX., 259.

† Journ. Chem. Soc. II., 265, 291: III., 30, 322, &c.

It was only in 1865 found that no difference exists between the two classes of hydrocarbons.

Dumas had previously shown that by acting with chlorine on marsh gas the compound CH_3Cl is formed, and Berthelot proved, 1857, that this body is identical with methyl chloride which, by heating with caustic potash, is easily converted into methyl alcohol. The author, by employing the same method, was able to show that the so-called ethyl-amyl $\left.\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\right\}$ yielded thus a heptyl chloride $C_7H_{15}Cl$, while both dimethyl and ethyl hydride are by the action of chlorine, converted into ethyl chloride. The views pronounced by Laurent and Gerhardt were thus fully confirmed, and the fact firmly established that Frankland's method of preparing the so-called radicals is a true synthesis. From the lower members of the paraffins we can build up the higher ones, and these can be converted into the alcohols, the fatty acids and many other derivatives, of which a number are found in organic nature.

But we must now go back again to 1847, when Frankland and Kolbe on one hand, and Dumas, Malaguti, and Leblanc on the other, found that by the action of alkalis and water on the cyanides of the alcohol radicals, they are converted into fatty acids containing one atom of carbon more than the alcohol, from which the cyanide has been obtained. This reaction became afterwards of great importance for the synthesis of organic bodies.

A similar synthesis had however been already effected in 1832, by Winkler, who by the combined action of hydrocyanic and hydrochloric acid on oil of bitter almonds or benzaldehyde C_7H_6O obtained mandelic or phenylglycollic acid $C_8H_8O_3$, which four years afterwards was more minutely examined by Liebig. By using the same method, Strecker succeeded as already mentioned, in 1850, in converting common aldehyde C_2H_4O into lactic acid $C_3H_6O_3$; but it was only many years later these reactions were recognised as synthetical processes.

These examples show that by the term organic synthesis we mean, not only the building up from the elements of compounds found in organic nature, but also the linking together of carbon atoms. To this class of synthesis belongs also the artificial preparation of oil of cinnamon from oil of bitter almonds, which Chiozza effected in 1856 by heating a mixture of the latter body with aldehyde and hydrochloric acid:

$$C_6H_5.COH + C_2H_4O = C_6H_5.C_3H_3O + H_2O.$$

Oil of cinnamon is the aldehyde of cinnamic acid $C_9H_8O_2$, which in the same year was prepared artificially by Bertagnini, who obtained it by heating oil of bitter almonds with acetyl chloride C_2H_3ClO:

$$C_6H_5.COH + CH_3.COCl = C_6H_5.C_3H_2.CO.OH + HCl.$$

Another important synthesis was effected by Wanklyn in 1858, who found that sodium ethide C_2H_5Na combines directly with carbon dioxide to form sodium propionate $C_2H_5.CO_2Na$.

In the next year Berthelot solved a problem long sought for by chemists, &c., *i.e.*, the direct union of carbon and hydrogen, which he effected by producing the electric arc between two carbon poles in a vessel through which pure hydrogen passed and thus obtained *acetylene* C_2H_2. This gas can readily be converted into *ethene* C_2H_4, *ethane* C_2H_6, and other compounds.

From that time the synthesis of organic bodies made more and more rapid progress. In this short sketch we can only mention some cases of more general interest.

We will begin with that of the primary alcohols which can be built up step by step. We have already seen that methyl alcohol $CH_3.OH$ can be converted into methyl cyanide or acetonitril $CH_3.CN$, which when heated with aqueous potash yields acetic acid, and by means of this reaction any alcohol can be transformed into a fatty acid containing one atom of carbon more. If therefore we are able to reduce such an acid to the alcohol containing the same number of carbon atoms in the molecule as the acid, the above problem is solved.

Now Williamson had already, in 1851, predicted that such an acid might be converted into its aldehyde by heating a mixture of calcium salts with calcium formiate; and, 1856, Piria,* as well as Limpricht,† proved this by experiment. Finally,

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* Ann. Chim. XLVIII., 113.

† Ann. Chem. Pharm. C., 104.

Wurtz* found, in 1862, that aldehydes combine with nascent hydrogen and form alcohols. Thus, acetic acid is transformed into propyl alcohol by the following reactions :

(1) $CH_3.CO.OH + CH.CO.OH = CH_3.COH + CO_2$

(2) $CH_3.COH + H_2 = CH_3.CH_2.OH$

(3) $CH_3.CH_2.OH + HI = CH_3.CH_2I + H_2O$

(4) $CH_3.CH_2I + KCN = CH_3.CH_2.CN + KI$

(5) $CH_3.CH_2.CN + 2H_2O = CH_3.CH_2.CO.OH + NH_3$

We have thus obtained propionic acid, which is then successively transformed into the aldehyde and propyl alcohol. From the latter we can obtain butyl alcohol, &c. Lieben and Rossi have by means of this reaction prepared the series of the normal primary alcohols up to octyl alcohol $C_8H_{18}O$.

The fatty acids can also be built up by another reaction which was discovered by Frankland and Duppa, and consists in replacing hydrogen in the methyl group of acetic acid by alcohol radicals; thus, by using ethyl we obtain butyric acid. We cannot discuss this reaction here more fully, and must refer the reader to modern textbooks.

The classical researches of Chevreul and of Berthelot have shown that fats consist chiefly of compound ethers, yielding, when saponified with an alkali, salts of fatty acids (soaps) and the triad alcohol glycerin $C_3H_5(OH)_3$.

Berthelot further found that a fat is again produced if its fatty acid is heated with glycerin; thus butyric acid yields tributyrin, a chief constituent of butter:

$$C_3H_5(OH)_3 + 3C_4H_7O.OH = C_3H_5(OC_4H_7O)_3$$

If therefore a method could be devised by which glycerin might be obtained from the elements, we should have a complete synthesis of many fats. This was done by Friedel and de Silva, who started with acetone C_3H_6O, which may be obtained synthetically in several ways (see p. 80). Nascent hydrogen converts it into secondary propyl alcohol $C_3H_7.OH$, which is easily converted into propene C_3H_6. This was combined with chlorine and the dichloride thus formed exposed to the action of iodine chloride, by which it was converted into the trichloride $C_3H_5Cl_3$, and this by heating with water under pressure yielded glycerin :

$$C_3H_5Cl_3 + 3H_2O = C_3H_5(OH)_3 + 3HCl$$

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* Compt. Rend. LIV., 914.

When glycerin is treated with iodine and phosphorus, it is converted into the compound C_3H_5I, which Berthelot and Luca discovered in 1854 and called allyl iodide. From this other allyl-compounds were prepared, some of which occur in nature, the sulphide $(C_3H_5)_2S$ being contained in the essential oil of garlic and many other plants having an alliaceous odour, while the essential oil of mustard consists chiefly of allyl thiocarbimide $C_3H_5N.CS$. Hofmann obtained afterwards a number of other thiocarbimides; almost all of them possess a very pungent smell, and therefore he gave to them the generic name the "mustard oils." He found that some of these occur in plants; thus, the essential oil of scurvy-grass consists of secondary butyl thiocarbimide.

Among other derivatives of the paraffins we find in nature three acids which are nearly related to each other:

Succinic acid ....$C_4H_6O_4$
Malic acid ....$C_4H_6O_5$
Tartaric acid ....$C_4H_6O_6$

The first of these was obtained synthetically by Maxwell Simpson; he heated ethene dibromide with potassium cyanide and acted upon the dicyanide thus formed with aqueous hydrochloric acid:

$$C_2H_4\left\{\begin{matrix}CN\\CN\end{matrix}\right. + 4H_2O + 2HCl = C_2H_4\left\{\begin{matrix}CO_2H\\CO_2H\end{matrix}\right. + 2NH_4Cl$$

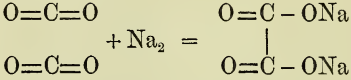
When we heat succinic acid with bromine, monobromosuccinic acid is formed, which as Kekulé has shown is converted into malic acid, when silver oxide is added to its boiling aqueous solution:

$$2C_2H_3Br(CO_2H)_2 + Ag_2O + H_2O = 2C_2H_3(OH)(CO_2H)_2 + 2AgBr_2$$

By the further action of bromine on monobromosuccinic acid we obtain dibromosuccinic acid, which as Kekulé, as well as Perkin and Duppa, found, is transformed into tartaric acid by boiling its silver salt with water, or the acid with quicklime (calcium hydroxide) and water:

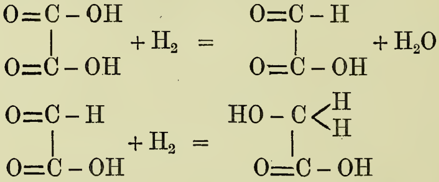
$$C_2H_2Br_2(CO_2H)_2 + Ca(OH)_2 = C_2H_2(OH)_2(CO_2H)_2 + CaBr_2.$$

Another interesting synthesis of tartaric acid was discovered by Debus, who obtained it from oxalic acid, which can be built up from the elements, as Kolbe has shown, in a very simple way: its sodium salt being formed by passing carbon dioxide over sodium heated to 360°.



$$\begin{array}{c} O{=}C{=}O \\ \\ O{=}C{=}O \end{array} + Na_2 = \begin{array}{l} O{=}C-ONa \\ \quad\;| \\ O{=}C-ONa \end{array}$$

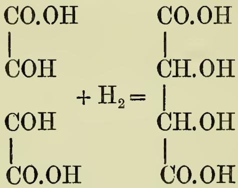
Nascent hydrogen converts oxalic acid into glyoxylic acid COH.CO.OH, and then into glycollic acid $CH_2(OH).CO.OH$:



$$\begin{array}{l} O{=}C-OH \\ \quad\;| \\ O{=}C-OH \end{array} + H_2 = \begin{array}{l} O{=}C-H \\ \quad\;| \\ O{=}C-OH \end{array} + H_2O$$

$$\begin{array}{l} O{=}C-H \\ \quad\;| \\ O{=}C-OH \end{array} + H_2 = \begin{array}{l} HO-C{<}\begin{smallmatrix}H\\H\end{smallmatrix} \\ \qquad\quad| \\ \quad O{=}C-OH \end{array}$$

Now Debus found that by acting on a solution of ethyl oxalate in spirits of wine with sodium amalgam, not only the above acids, but also tartaric acid is formed, which is not difficult to explain, as the two atoms of hydrogen can enter the glyoxylic acid one after the other; if only one enters we have an unsaturated molecule; of these two can combine and form tartaric acid:



$$\begin{array}{l} CO.OH \\ | \\ COH \\ \\ COH \\ | \\ CO.OH \end{array} + H_2 = \begin{array}{l} CO.OH \\ | \\ CH.OH \\ | \\ CH.OH \\ | \\ CO.OH \end{array}$$

Thus we see that a few simple steps lead us from carbon dioxide, one of the principal foods of plants, to a complex organic acid, and still more interest is imparted to this by the fact that glycollic and tartaric acid are found together in grapes and in the leaves of the Virginian creeper.

That such organic acids might be built up from carbon dioxide had been foreseen by Liebig, as the following passages from his Letters on Chemistry will show:—

"The carbon of all parts and constituents of vegetables, and through vegetables of animals, is derived from *carbonic acid;* all the hydrogen of non-nitrogenised organic bodies (sugar, starch, woody fibre, gum, oils, &c.) is derived from water . . .

"No part of a vegetable or animal organism contains, for one atom of carbon, more than two atoms of another element. The great majority of organic bodies contain, for one atom of carbon, less than two other atoms.*

"All the constituents of organisms are formed of atoms of carbonic acid, more or less modified, or of groups of such modified carbonic acid atoms. These atoms, or groups of atoms, have been produced, under the influence of solar light, from the carbonic acid absorbed by the roots and leaves of plants. The change is the result of a separation and extrusion of part of the oxygen of the carbonic acid atoms, in the place of which oxygen there is taken up hydrogen, or hydrogen and nitrogen. Viewed in the simplest way, an atom of grape-sugar, for example, may be regarded as an atom of carbonic acid, in which one oxygen atom has been removed by one hydrogen atom. . . . .

"The acids so widely distributed in vegetables, such as oxalic acid (in oxalis, rumex, rheum, &c.), malic acid (in most unripe fruits), citric acid (in the lemon, lime, orange, &c.), and others, stand to each other, and to carbonic acid, in a relation as simple as that between carbonic acid and grape-sugar. By the separation from a group of two carbonic acid atoms, of one oxygen atom, oxalic acid is formed. If to a group of two atoms of oxalic acid two atoms of hydrogen be added, and from the whole two atoms of oxygen be removed, malic acid is the result. We have every reason to believe that by a continuance of such changes sugar, gum, starch, and woody fibre are formed, and that they (the acids) are links in a chain exhibiting the gradual conversion of the atom of carbonic acid into sugar and the other more complex organic atoms."

Chemists have not been able yet to effect these latter changes, but there is no doubt that they are possible, inasmuch as we are able to convert sugar by the inverse reactions into tartaric, malic, and oxalic acids, &c.

On looking at the graphic formula of tartaric acid we observe that it contains two asymmetric carbon atoms, and it has been known for a considerable time that tartaric acid is an optically active substance, but it is always accompanied by an isomeride, which has been called racemic acid, and which differs from tartaric acid chiefly by its having no action on the polarised light.

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* It is perhaps hardly necessary to state that Liebig meant by an atom of a compound that which we call now a molecule, and that he used the equivalent numbers: $H=1$; $O=8$; $C=6$.

Pasteur found that by converting racemic acid into ammonium sodium racemate $C_4H_4(NH_4)NaO_6$, and allowing the solution to crystallise slowly, two kinds of crystals are obtained, each of them containing certain small faces equal in number and form, but developed on opposite sides of the two crystals, so that one looks like the image of the other reflected from a mirror. On carefully separating these two kinds of crystals and isolating them from the acids, it was found that one was common tartaric or dextrotartaric acid, as it turns the plane of the polarisation to the right, as strongly as the second does it to the left, and which was therefore called laevotartaric acid. On dissolving equal parts of them and evaporating the solution, inactive racemic acid again crystallises out.

The tartaric acid which has been prepared artificially was first believed to be racemic acid, inasmuch as it has no action on the polarised light, but it was found that it cannot be separated by the method described into the two active modifications. We do not know the reason why organic bodies, when produced in nature, are often optically active, while the same compound if prepared artificially, are not. However, in the case of tartaric acid, means have been found by which the synthetical compound can be converted into the modifications occuring in nature. Jungfleisch found that, when the inactive acid is heated with water in closed vessels to 175°, it is converted into racemic acid. By means of the reactions above described he obtained from ethene all the four modifications of tartaric acid.

CHAPTER XI.

SYNTHESIS OF AROMATIC BODIES.—BENZENE.—BENZOIC ACID.—OIL OF BITTER ALMONDS.—SALICYLIC ACID.—CUMARIN.—VANILLIN.—ALIZARIN.

A great number of syntheses of aromatic compounds is also known, but here again a few only possessing a more general interest can be described.

Berthelot found that on heating acetylene to a dull red heat it is polymerised, the chief product consisting of benzene C_6H_6.

As we have already seen, all other aromatic compounds are derivatives of this hydrocarbon; its homologues being formed by the substitution of alcohol radicals for hydrogen. This synthesis may be effected, as Fittig and Tollens found, by a method quite similar to that which Wurtz used for obtaining some of the paraffins.

By the action of bromine on benzene we obtain bromobenzene, which, when treated with methyl iodide and sodium, yields methyl-benzene or toluene :—

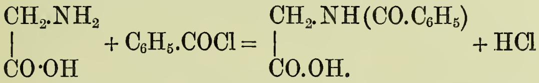
$$C_6H_5Br + CH_3I + Na_2 = C_6H_5.CH_3 + NaBr + NaI.$$

If we use ethyl iodide in the place of the methyl compound, we obtain ethyl-benzene $C_6H_5.C_2H_5$, &c.

On passing carbon dioxide into a mixture of bromobenzene and sodium, Kekulé obtained the sodium salt of benzoic acid :—

$$C_6H_5Br + CO_2 + Na_2 = C_6H_5.CO_2Na + Br.$$

This acid is also formed by the oxidation of toluene ; phosphorus chloride converts it into benzoyl chloride, which, by the action of amidacetic acid, is changed into hippuric acid, a normal constituent of the urine of the graminivora :



$$\begin{array}{l}CH_2.NH_2\\ |\\ CO\cdot OH\end{array} + C_6H_5.COCl = \begin{array}{l}CH_2.NH(CO.C_6H_5)\\ |\\ CO.OH.\end{array} + HCl$$

Benzoic aldehyde $C_6H_5.COH$ forms the chief constituent of oil of bitter almonds; it is now prepared on a large scale by treating boiling toluene with chlorine until benzylene dichloride $C_6H_5.CHCl_2$ is formed, which is then heated with mercuric oxide :—

$$C_6H_5.CHCl_2 + HgO = C_6H_5.CHO + HgCl_2.$$

The essential oils of common cress and of the garden-nasturtium (Tropaeolum majus) consist principally, as Hofmann has shown, of benzyl cyanide or phenylacetonitril $C_6H_5.CH_2.CN$, while that of watercress contains the homologous phenylpropionitril $C_6H_5.C_2H_4.CN$. Both are readily prepared artificially from toluene and ethylbenzene, by replacing in their alcohol radicals first one atom of hydrogen by chlorine, and then heating the monochlorides, thus formed, with potassium cyanide.

When benzene is dissolved in strong sulphuric acid it is converted into benzenesulphonic acid. On fusing the potassium salt of the latter with potash, phenol or carbolic acid is formed, a compound occurring in large quantities in coal-tar and in smaller ones in urine and castoreum :

$$C_6H_5.SO_3K + KOH = C_6H_5.OH + K_2SO_3.$$

From phenol we can obtain salicylic acid, which occurs in several plants; its methyl ether forms the chief constituent of oil of winter green. Kolbe and Lautemann found that when carbon dioxide is passed into phenol in which sodium is dissolving, salicylic acid is formed :

$$C_6H_5.ONa + CO_2 = C_6H_4\left\{\begin{array}{l}OH\\ CO_2Na.\end{array}\right.$$

Kolbe afterwards simplified this method by dissolving phenol in caustic soda, evaporating down and heating the residue in a current of carbon dioxide. He also found that the above equation does not correctly interpret the reaction taking place, which is as follows :

$$2C_6H_5.ONa + CO_2 = C_6H_4\left\{\begin{array}{l}ONa\\ CO_2Na\end{array}\right. + C_6H_5.OH$$

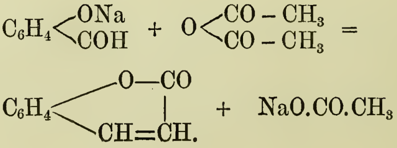
One half of the phenol is set free again, and the other half converted into the so-called basic sodium salicylate.

According to this process salicylic acid is now largely manufactured, as it was found to possess powerful antiseptic and medical properties.

Its aldehyde $C_6H_4(OH)COH$ exists in the essential oil of different species of *Spiræa* (the meadow-sweet, &c.); it is also easily obtained from phenol by Reimer and Tiemann's method, *i.e.*, by acting with chloroform on a solution of phenol in caustic soda :

$$C_6H_5.OH + CHCl_3 + 3NaOH = C_6H_4\left\{\begin{array}{l}OH\\ CHO\end{array}\right. + 3NaCl + 2H_2O.$$

Perkin has transformed salicyl aldehyde into cumarin, which exists in sweet woodruff, the sweet-scented vernal grass, tonka-beans, and other aromatic plants. He effected this synthesis by heating the sodium compound of salicyl aldehyde with acetic anhydride :



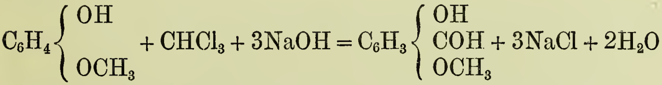
$$C_6H_4\begin{array}{l}\diagup ONa\\ \diagdown COH\end{array} + O\begin{array}{l}\diagup CO-CH_3\\ \diagdown CO-CH_3\end{array} =$$

$$C_6H_4\begin{array}{l}\diagup O—CO\\ \quad\quad\ \ |\\ \diagdown CH{=}CH.\end{array} + NaO.CO.CH_3$$

Oil of cinnamon owes its pleasant smell to the presence of cinnamaldehyde $C_6H_5.C_2H_2.COH$. The synthesis of this body has already been described, as well as that of cinnamic acid, which is also easily formed by oxidation of the aldehyde, and occurs in liquid styrax, balsam of Peru, and other similar bodies.

The odoriferous principle of vanilla consists, as Tiemann has shown, of methylprotocatechuic aldehyde $C_6H_3(OH)(OCH_3)COH$. Its synthesis does not offer any difficulty. We start from phenol, which by the action of iodine and iodic acid in presence of an alkali yields the three isomeric iodophenols; these can be easily separated. On distilling the product with steam, liquid orthoiodophenol $C_6H_4I.OH$ passes over first. When this is fused with potash it is converted into orthodihydroxybenzene $C_6H_4(OH)_2$, a compound better known by the name of pyrocatechin, as it was first obtained by the dry distillation of catechu. On heating it with methyl iodide and potash in the required proportions, we obtain the monomethyl-ether $C_6H_4(OH)OCH_3$, which has been called guaiacol, because it exists in the products of the dry distillation of guaiac resin; it also forms a component of creosote.

The conversion of guaiacol into vanillin is perfecty analogous to the formation of salicylaldehyde from phenol. Guaiacol is dissolved in caustic soda and the solution heated with chloroform:



$$C_6H_4\left\{\begin{matrix} OH \\ \\ OCH_3 \end{matrix}\right. + CHCl_3 + 3NaOH = C_6H_3\left\{\begin{matrix} OH \\ COH \\ OCH_3 \end{matrix}\right. + 3NaCl + 2H_2O$$

The formation of the beautiful aniline colours is also a synthetical process. E. and O. Fischer have found that these compounds, which are obtained by the oxidation of a mixture of aniline $C_6H_5.NH_2$, and some of its higher homologues are derivatives of triphenyl-methane $C_{19}H_{16}$, a hydrocarbon, which Kekulé and Franchimont first prepared by the following process. When bromobenzene C_6H_5Br is treated with sodium amalgam $HgNa_2$, we obtain mercury diphenyl $Hg(C_6H_5)_2$ and on heating this with benzylene chloride the above hydrocarbon is formed:

$$C_6H_5.CHCl_2 + Hg(C_6H_5)_2 = CH(C_6H_5)_3 + HgCl_2.$$

On oxidation it yields a tertiary alcohol, triphenylcarbinol $HO.C(C_6H_5)_3$, which fuming nitric acid converts into the trinitro compound $HO.C(C_6H_4.NO_2)_3$. Nascent hydrogen acts on this as upon other nitro-compounds; the nitroxyl-groups being converted into amidogen, and thus pararosaniline $HO.C(C_6H_4.NH_2)_3$ is formed, which is the most simple compound of the rosaniline group or the bodies known as the aniline colours.

Numerous other examples might be quoted, but the above will be sufficient to give an idea how far organic synthesis has advanced.

We shall therefore conclude with the history of the syntheses of some of the most important natural colouring matters, those of madder-root and of indigo.

Madder-root contains several colouring matters; the most important of these was discovered in 1826 by Colin and Robiquet, who called it *alizarin*, because the oriental name of madder was alizari.* The formula of this compound remained, however, doubtful till 1868, although several eminent chemists investigated this subject.

E. Schunck calculated from the results of his analyses the formula $C_{14}H_{10}O_4$; he found, 1848, that by oxidation it yields an acid which he called alizaric acid, but Gerhardt pointed out that this body was probably identical with phthalic acid $C_8H_6O_4$ which Laurent had obtained by oxidising naphthalene $C_{10}H_8$, a hydrocarbon occurring in coal tar. This view was confirmed by Strecker and Wolff in 1850, who, from this fact, coupled with the results of their analysis, assumed that alizarin was a derivative of naphthalene and had the formula $C_{10}H_6O_3$, which was generally accepted, although Schunck in 1852 brought forward fresh proofs for the correctness of his formula.

Strecker and Wolff made experiments for the purpose of converting naphthalene into alizarin, but in vain. Other chemists afterwards succeeded in transforming this hydrocarbon into a compound having the above formula, but it turned out to be quite different from alizarin, and was regarded as an isomeride.

Strecker, who recommenced his researches on alizarin later on, found, 1866, that its formula was $C_{14}H_8O_4$, but he did not publish his analytical data until after the discovery of artificial alizarin had been made in 1868 by Gräbe and Liebermann.

Baeyer had, 1866, shown that phenols and similar compounds lose their oxygen on their vapour being passed over finely divided zinc or so-called zinc-dust; common phenol yielding benzene :

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* Littré's Dict. Suppl.: "Espagnol, alizari, de l'arabe asāra, qui signifie le suc extrait d'un végétal par compression." My friend Professor Theodores has informed me that this word comes from *azara*, "to press or to squeeze."

$$C_6H_6O + Zn = C_6H_6 + ZnO.$$

Gräbe and Liebermann applied this reaction to alizarin, and thus obtained a hydrocarbon which had been discovered by Dumas and Laurent in coal-tar, and was afterwards more carefully examined by Fritzsche and by Anderson, who called it *anthracene* $C_{14}H_{10}$. From this it would appear likely that Schunck's formula expressed the true constitution of alizarin, but Gräbe and Liebermann adopted, before Strecker had published his results, the formula $C_{14}H_8O_4$, partly for theoretical reasons, partly because on comparing the analyses which had been published, they found that those made with the purest sublimed alizarin agreed best with this formula, even the first made by Robiquet, at whose time the exact atomic weight of carbon was not known, in consequence of which he calculated a very complicated formula. That Schunck found a little too much hydrogen is easily accounted for, as in the old method of analysis traces of moisture could not be excluded, and the difference between the hydrogen in the two formulæ being only 0·8 %, while Schunck found only 0·4 % too much. Moreover, it is not easy to obtain a perfectly pure alizarin, so that the substance analysed might contain small quantities of compounds richer in hydrogen.

But how is it that on heating a compound containing only eight atoms of hydrogen with zinc-dust, a hydrocarbon is formed which contains ten? The explanation for this is, that the finely divided metal always retains zinc hydroxide $Zn(OH)_2$, which at a gentle heat is resolved into zinc oxide and water; the latter easily acts on the zinc, forming the oxide and setting hydrogen free; anthracene being thus formed according to the equation :

$$C_{14}H_8O_4 + H_2 + 4Zn = C_{14}H_{10} + 4ZnO.$$

As soon as Gräbe and Liebermann had established that alizarin is a derivative of anthracene they endeavoured to obtain it from this hydrocarbon.

Laurent had already found that anthracene by oxidation yields the compound $C_{14}H_8O_2$, which he called anthracenuse, and which afterwards was further examined by Anderson, who named it oxanthracene. This compound is an exceedingly stable body, being hardly attacked by any oxidising agents, by which it differs from alizarin; the latter contains two atoms of oxygen more, which, as its whole chemical character shows, must be present in the form of hydroxyl.

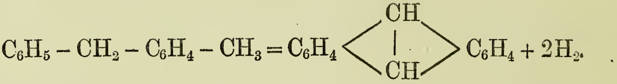
Starting from these premises, Gräbe and Liebermann succeeded in replacing two atoms of hydrogen in oxanthracene, or as they called it anthraquinone, by hydroxyl. They effected this by heating the quininone with bromine in sealed tubes, and thus obtained dibromanthraquinone, which on fusing with caustic potash was converted into alizarin:

$$C_{14}H_6Br_2O_2 + 2KOH = C_{14}H_6(OH)_2O_2 + 2KBr.$$

Thus for the first time a colouring matter hitherto only produced in plants was prepared artificially. Moreover, it was a complete synthesis, as Limpricht had two years previously obtained anthracene synthetically from benzyl chloride; this when heated with water to 180° yields anthracene, together with another hydrocarbon and hydrochloric acid:

$$4C_6H_5.CH_2Cl = C_{14}H_{10} + C_{14}H_{14} + 4HCl.$$

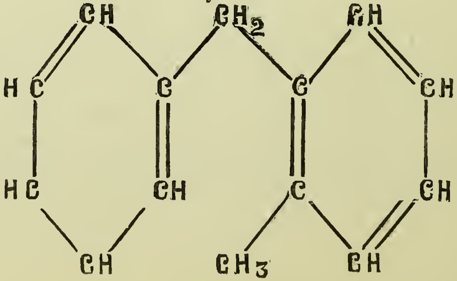
The second hydrocarbon was afterwards recognised by van Dorp as benzyl-toluene $C_6H_5.CH_2.C_6H_4.CH_3$, which Zincke had previously obtained by replacing in toluene one atom of hydrogen by benzyl; van Dorp found further that this hydrocarbon is at a red heat resolved into anthracene and free hydrogen. From these reactions as well as others, the constitution of anthracene has been ascertained; its formation from benzyl-toluene being explained by the following equation:



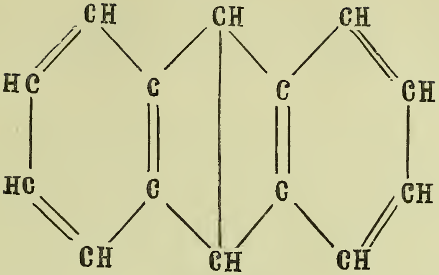
$$C_6H_5 - CH_2 - C_6H_4 - CH_3 = C_6H_4 \left< \begin{matrix} CH \\ | \\ CH \end{matrix} \right> C_6H_4 + 2H_2.$$

The dissected formulæ of these two hydrocarbons are the following:

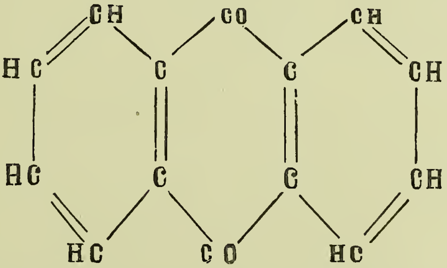
Benzyl-toluene.



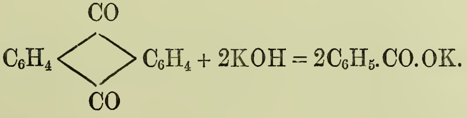
Anthracene.



Anthraquinone is not only obtained by the oxidation of anthracene, but also from tolyl-phenyl ketone $C_6H_5.CO.C_6H_4.CH_3$, which is formed as the first product of the oxidation of benzyl toluene. On passing the vapour of this ketone over heated lead oxide anthraquinone is formed which has the following constitution:



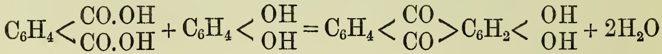
That anthraquinone has this graphic formula is proved by the fact that by fusing it with potash it yields two molecules of benzoic acid



$$C_6H_4\left\langle\begin{array}{c}CO\\CO\end{array}\right\rangle C_6H_4 + 2KOH = 2C_6H_5.CO.OK.$$

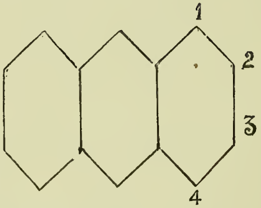
We have given these formulæ for several reasons; one of them is to point out that 10 isomeric derivatives of anthraquinone having the formula $C_{10}H_6O_2(OH)_2$ can exist, and these are now all known. But all of these, with the exception of alizarin, are either no colouring matters or only such of very little value. Is it therefore not most remarkable that Gräbe and Liebermann, in their first attempt to prepare alizarin from anthraquinone, obtained this body, instead of one of its isomerides?

Another question is, why is alizarin such a valuable dye-stuff, when the other dioxyanthraquinones are not? This must certainly depend on its chemical constitution, as we know that between this and the physical properties of bodies many relations exist. Thus among the coloured disubstitution-products of benzene, the ortho-compounds have always the most intense colour. Now, alizarin is an ortho-compound, which has been proved by Baeyer and Caro, who obtained it by heating pyrocatechin (orthodihydroxybenzene) with phthalic acid and sulphuric acid, the latter acting as dehydrating agent—



$$C_6H_4<\begin{matrix}CO.OH\\CO.OH\end{matrix} + C_6H_4<\begin{matrix}OH\\OH\end{matrix} = C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2<\begin{matrix}OH\\OH\end{matrix} + 2H_2O$$

But the question is thus not quite settled, as a look at the following diagram will show:



In alizarin the two hydroxyls can either occupy the position 1, 2 or 2, 3. The same chemists however have shown, that by using in the above reaction phenol in the place of pyrocatechin two isomeric monhydroxyanthraquinones $C_{14}H_5O_2(OH)$ are formed; it is obvious that in one of these the hydroxyl occupies the position 1, and in the second the position 2. But as both, when fused with potash, exchange one atom of hydrogen for hydroxyl, and yield alizarin, the hydroxyls in the latter must be in the position 1, 2.

The same has been proved in another way, which is also of great interest, because it shows the synthesis of two other colouring matters existing in madder-root. One of these, which is called purpuroxanthin, is isomeric with alizarin, and occurs only in small quantity, but is easily obtained by the reduction of purpurin $C_{14}H_5(OH)_3O_2$, which exists in the root in larger quantity. A third isomeride of alizarin was obtained by Baeyer, who called it quinizarin, because it is formed by heating hydroquinone (paradihydroxybenzene) with phthalic acid and sulphuric acid.

Now alizarin and its two isomerides, as well as purpurin, are converted by strong oxidising agents into phthalic acid, $C_6H_4(CO_2H)_2$, proving that they contain the hydroxyls in the same aromatic nucleus. Weaker oxidising agents transform alizarin, purpuroxanthin, and quinizarin into purpurin. But the hydroxyls of the latter can only be in the position 1,2,4 = 1,3,4 because quinizarin is a para-compound. But as alizarin is a ortho-compound, it follows that the positions of the hydroxyls in the three dihydroxyanthraquinones are the following:

Alizarin.	Purpuroxanthin.	Quinizarin.
1,2 = 3,4	1,3 = 2,4	1,4

Gräbe and Liebermann's original method was not adapted for obtaining alizarin on a large scale. But in conjunction with H. Caro they succeeded in devising commercially practical processes, and so did W. H. Perkin at the same time. This is not the place to describe the manufacture of alizarin, only the principle may be shortly touched upon. We have already seen that when benzene is dissolved in sulphuric acid it is converted into benzenesulphonic acid, which, when fused with an alkali, yields phenol. On heating anthraquinone with sulphuric acid several sulphonic acids are produced at the same time. These are not separated, but fused with soda, a consequence of which is, that commercial alizarin contains more or less of several other hydroxyanthraquinones. Of these one must be mentioned; it was discovered by Perkin, who named it anthrapurpurin, because it is an isomeride of purpurin $C_{14}H_5O_2(OH)_3$.

Anthrapurpurin is a most valuable dye-stuff, producing on alumina mordants most brilliant shades resembling turkey-red, while alizarin dyes bluish pinks and reds, and a mixture of both colouring matters gives intermediate shades.

The manufacturers of artificial alizarin now separate the colouring matters more or less completely according to the colour demanded.

No difficulty was apparently encountered in explaining the formation of anthrapurpurin; it was regarded as a derivative of an anthraquinone-trisulphonic acid $C_{14}H_5O_2(SO_3H)_3$, which easily could have been produced together with disulphonic acid, which, as it was believed, yielded alizarin.

But when the subject was more minutely examined this was found not to be the case, inasmuch as the sulphonic acids which are used are a mixture of a monosulphonic and two isomeric disulphonic acids, while the product obtained by fusing with soda contains, besides alizarin and anthrapurpurin, not only isomerides of these but also regenerated anthraquinone and a monohydroxyanthraquinone.

This mystery was however soon cleared up. Alizarin is a derivative of the monosulphonic acid, which when fused with potash is converted into monohydroxyanthraquinone. When the temperature of the melt increases, soda exerts, as in other cases, at the same time on oxidising and a reducing action, alizarin and anthraquinone being found at the same time :

$$2C_{14}H_7O_2(OH) = C_{14}H_6O_2(OH)_2 + C_{14}H_8O_2.$$

Anthrapurpurin is produced by a very similar reaction ; one of the disulphonic acids being first converted into isoanthraflavin, one of the isomerides of alizarin, and this is then further acted upon by soda, with the formation of anthrapurpurin and anthraquinone or other products of reduction.

The manufacturer wishes, of course, to avoid the formation of the latter compounds as much as possible. This is done to some extent by adding an oxidising agent to the fusing mass. R. S. Dale and the author had previously shown that alizarin may be obtained by dissolving anthracene, instead of anthroquinone, in hot sulphuric acid, and fusing the sulphonic acids thus formed with soda and potassium chlorate or other suitable oxidising agents.*

The formation of alizarin and anthrapurpurin, which appears to be formed at the same time, under the above conditions, is easily explained. The anthracenesulphonic acids are first converted into the corresponding hydroxanthracenes, and these then oxidised by the potassium chlorate to hydroxanthraquinones.

The facility with which the chlorate acts has then induced the alizarin manufacturers using the old process to employ it, in order to avoid, as much as possible, the formation of products of reduction.

Although the discovery of artificial alizarin has been made only eleven years, it has already produced a complete revolution in calico-printing, turkey-red dyeing, the manufacture of madder preparations, and the cultivation of madder. A friend of the author's was travelling a few years ago in the south of France and came to Avignon; after he had seen all the sights of this interesting old town he requested his *valet de place* to take him to the madder plantations, Avignon madder having always been considered one of the best in the market. The reply was: "We don't grow any more;" and on asking why, he was told: "Monsieur, it is now all made by machinery!"

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*Patent Jan. 24, 1870.

CHAPTER XII.

SYNTHESIS OF INDIGO.—INDIGO BLUE.—INDIGOPURPURIN.—PROBLEMS STILL TO BE SOLVED.—CONCLUSION.

Another brilliant discovery is that of the synthesis of *indigo*, the "Indian colour," which is obtained from different species of *Indigofera* and other plants, and was known to the ancients. It is mentioned by Dioscorides and Pliny. The latter says:—*Ab hoc maxima auctoritas Indico. Ex India venit, arundinum spumae adhaerescente limo; quum teritur, nigrum; at in diluendo mixturam purpurae caeruleique mirabilem reddit. Alterum genus ejus est in purpurariis officinis innatans cortinis, et est purpurae spuma. Qui adulterant, vero Indico tingunt stercora columbina, aut cretam Selunisiam, vel annularium vitro inficiunt. Probatur carbone. Reddit enim, quod sincerum est, flammam excellentis purpurae.*

The ancients used it only as a pigment, not knowing how to make it soluble, and thereby to avail themselves of it for dyeing. It is also mentioned by the Arabians, but only since the discovery of the sea passage to India it has become generally known in Europe. Its use as a dye was however greatly retarded by the opposition it met from the large vested interests of the cultivators of woad (*Isatis tinctoria*), the European indigo-plant. The English, French, and several German governments were induced by them to promulgate severe enactments against it. Thus Henry IV. of France issued an edict, condemning to death anyone who used that pernicious drug called "devil's food."

The employment of woad was however gradually superseded by that of indigo, and as soon as organic chemistry had advanced far enough, chemists commenced to examine this valuable dye-stuff. The literature on this subject is exceedingly large; of the numerous researches, we can here mention only those bearing directly on our subject, and this we will do in chronological order.

The colouring matter of indigo, which has been called indigo-blue or indigotin, was first obtained in the pure state by O'Brien, who states in his treatise "On Calico Printing," 1789, that on heating indigo the colouring matter will form a purple vapour (as Pliny already had mentioned), which will condense as a blue powder, while the other substances contained in the commercial product remain behind. As soon as organic analysis had far enough advanced indigotin was analysed with the result that its most simple formula is C_8H_5NO, which was subsequently doubled for several reasons; its vapour density has only been determined quite recently by Sommaruga, who thus proved that its molecular formula is really $C_{16}H_{10}N_2O_2$.

On distilling indigo with caustic potash, Fritzsche obtained, 1840, a basic oil which he called *aniline*, from "anil," by which name the Portugese introduced indigo into Europe. The word is Arabic, and means "the blue."* In the next year he obtained by boiling indigo with caustic soda and black oxide of manganese, a compound which he called anthranilic acid, and which is now known as orthamidobenzoic acid $C_6H_4(NH_2)CO_2H$; he also found that by heat this acid is resolved into carbon dioxide and aniline. At about the same time Erdmann and Laurent independently studied the action of oxidising agents on indigo and obtained isatin $C_8H_5NO_2$, which is not a colouring matter and crystallises in reddish brown prisms. The further examination of this compound yielded most interesting results, but as not being connected with the present subject, we cannot discuss them, but must proceed at once to 1865, when Baeyer and Knop found that by bringing together isatin, sodium amalgam and water, the nascent hydrogen combines with the former, dioxindol $C_8H_7NO_2$ being formed, a solid crystallising in yellow needles. This is easily further reduced, in an acid solution by hydrogen in the nascent state, to oxindol C_8H_7NO, forming colourless needles. On passing its vapour over red zinc dust it loses its oxygen and is converted into indol C_8H_7N, which is also a colourless crystalline compound and a very interesting body, inasmuch as it is also formed as Nencki and Kühne have shown in pancreatic digestion, and contained in the excrements, which owe their characteristic smell to the presence of this body.

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* An eminent oriental scholar has informed me that the name of the river Nile is probably of the same origin, one of its branches being still called the "blue Nile," a pleonasm!

In 1869, Baeyer and Emmerling obtained indol from cinnamic acid, which as we have seen can be formed by synthesis. Cinnamic acid is first treated with nitric acid, and the orthonitrocinnamic acid, thus obtained, heated with iron filings and caustic potash, to remove oxygen and carbon dioxide:

$$C_8H_6(NO_2).CO_2H = C_8H_7N + O_2 + CO_2.$$

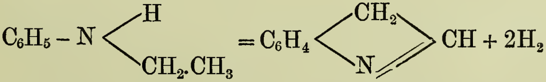
For theoretical reasons however they then doubled the formula of indol.

The same chemists discovered, 1870, a method by which isatin is by the removal of oxygen reduced to indigo blue. By heating it with a mixture of phosphorus trichloride, acetyl chloride, and phosphorus to 75-80° they obtained a green liquid, which when poured in water deposited, on standing exposed to the air, a blue precipitate containing indigo blue, together with another, probably isomeric, colouring matter, called indigo purpurin.

It has been known for some time that urine sometimes deposits a blue powder, which consists of indigotin. Jaffé, in 1870, found that he could produce this by the subcutaneous injection of indol, and Nencki, who confirmed this observation in 1875, observed that when indol suspended in water is acted upon by ozonised air, it is oxidised to *indigotin*, but the yield is small on account of its readily undergoing further oxidation.

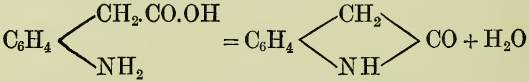
The synthesis of indigo was thus completed, but chemists were not satisfied with it, as neither the molecular weights nor the constitution of the bodies belonging to the indigo group had been made out; the researches were therefore continued, and Nencki found, 1876, by determining the vapour density of indol that its molecular formula was really C_8H_7N.

In the next year Baeyer and Caro found a very simple and elegant synthesis of indol by passing the vapour of ethylaniline through a red-hot tube:



$$C_6H_5-N\left<\begin{matrix}H\\CH_2.CH_3\end{matrix}\right. = C_6H_4\left<\begin{matrix}CH_2\\N\end{matrix}\right>CH + 2H_2$$

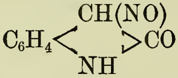
Baeyer succeeded then in 1878 to obtain oxindol from phenylacetic acid $C_6H_5.CH_2.CO_2H$, which can be prepared synthetically by different methods. Cannizzaro obtained it in 1855, as already stated, by treating benzyl chloride $C_6H_5.CH_2Cl$ with potassium cyanide and decomposing the nitril $C_6H_5.CH_2.CN$ thus obtained with caustic potash. Baeyer found now that this acid is readily converted into orthonitrophenylacetic $C_6H_4(NO_2)CH_2.CO_2H$, which, by the action of nascent hydrogen, yields the corresponding amido-compound. But this, like other ortho-compounds, readily loses water, forming an anhydride which is oxindol:



$$C_6H_4\left\langle\begin{matrix}CH_2.CO.OH\\ NH_2\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CH_2\\ NH\end{matrix}\right\rangle CO + H_2O$$

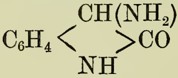
This compound, as Baeyer and Knop had already found, is converted by the action of nitrous acid into nitrosoxindol $C_8H_6(NO)NO$, which nascent hydrogen transforms into amidoxindol $C_8H_6(NH_2)NO$, and this yields on oxidation isatin, the graphic formulæ of these compounds being

Nitrosoxindol.



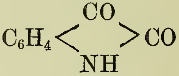
$$C_6H_4\left\langle\begin{matrix}CH(NO)\\ NH\end{matrix}\right\rangle CO$$

Amidoxindol.



$$C_6H_4\left\langle\begin{matrix}CH(NH_2)\\ NH\end{matrix}\right\rangle CO$$

Isatin.



$$C_6H_4\left\langle\begin{matrix}CO\\ NH\end{matrix}\right\rangle CO$$

It has already been stated that in the transformation of isation into indigo blue another purple colouring colour is formed.

In order to avoid the formation of this indigopurpurin, and also for the purpose of studying the reaction more carefully, Baeyer tried other methods. He found that phosphorus pentachloride converts isatin into the compound C_8H_4ClNO, which nascent hydrogen converts into indigo blue $C_{16}H_{10}N_2O_2$. Baeyer is proceeding with his researches which undoubtedly will soon clear up the constitution of the latter compound.

As far back as 1869, Kekulé predicted isatin to possess the constitution which it has been proved to have by Baeyer's experiments, and two of Kekulé's pupils, Claisen and Shadwell, have found a very simple synthesis of it. By acting with phosphorus chloride on orthonitrobenzoic acid they obtained the compound $C_6H_4(NO_2)COCl$, which they heated with silver cyanide; the nitril $C_6H_4(NO_2).CO.CN$ thus formed, yielded by the action of caustic potash orthonitrophenylglyoxylic acid $C_6H_4(NO_2).CO.CO.OH$, and this is converted by nascent hydrogen into the amido-compound, which, like other ortho-compounds, loses water and yields isatin.*

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* Ber. deutsch. chem. Ges. XII., 350.

The artificial preparation of indigo has so far merely a theoretical interest; whether the time will come when simplified methods will admit of its manufacture on a large scale remains to be seen. But even if not, the indigopurpurin, which is always formed together with the blue, may become of importance as a colouring matter. This body, as Schunck has shown, is identical with his *indigorubin*, which always occurs, but in a small quantity only, in indigo. Schunck has traced the formation of this beautiful purple colour in *Polygonum tinctorium*, a plant used in China and Japan for the preparation of indigo. He has cultivated it for several years, and found that the young plants do not contain a trace of it. It can only be obtained from plants having attained an advanced stage of development. It dyes under the same conditions as indigotin does; but while the latter produces a dull, dark blue, indigorubin dyes a fine purple shade. Schunck, who is an authority on these matters, is of the opinion that if it could be obtained in quantity, it would be a most valuable addition to the colouring matters now in use.

In his "Letters on Chemistry," Liebig expresses himself as follows on inorganic synthesis: "But of all the achievements of inorganic chemistry the artificial preparation of lapis lazuli was the most brilliant and the most conclusive. This mineral, as presented to us by nature, is calculated powerfully to arrest our attention by its beautiful azure-blue colour, its remaining unchanged by exposure to air or to fire, and furnishing us with a most valuable pigment, ultramarine."

"Ultramarine was dearer than gold; it seemed impossible to form it, for analysis had sought in vain for the colouring ingredient. It was shown to be composed of silica, alumina, and soda, with sulphur and a trace of iron, none of which are blue; and no other body had been detected in it to which its colour could be ascribed. Yet now, simply by combining in the proper proportions, as determined by analysis, silica, alumina, soda, iron, and sulphur, thousands of pounds weight* are manufactured from these ingredients; and this artificial ultramarine is even more beautiful than the natural, while for the price of a single ounce of the latter we may now obtain many pounds of the former."

"With the production of artificial lapis lazuli, the formation of mineral bodies ceased to be a scientific problem to the chemist."

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* To-day we may say thousands of hundred-weights.

In organic chemistry we are however not yet so far advanced. Many problems have still to be solved, such as the artificial preparation of the compounds forming ingredients of our daily food: sugar, starch, gum, &c. Not only the empirical formulæ of these substances are known, but, in case of several, the molecular and even graphic formulæ also. We may therefore hope to obtain at least the latter bodies by the synthetical method.

But it is quite different with another class of bodies which form most important ingredients of our food, the albuminous compounds. All which we know of these is their percentage composition, and further, that they must have a very high molecular weight and contain the carbon atoms linked together partly as in the group of the fatty and partly as in the group of the aromatic bodies. How complicated the composition of the albuminous compound is appears from the most simple formula of purified albumin (the white of egg) which, according to Lieberkühn, consists of $C_{72}H_{112}N_{18}SO_{22}$.

Kekulé, in discussing lately "the scientific aims and achievements of chemistry"* says: "The hypothesis of chemical quantivalence further leads to the supposition that also a relatively large number of single molecules may, through polyvalent atoms, combine to *net-like*, and if we may say so, *sponge-like* masses, in order thus to produce those molecular groups which resist diffusion, and which, according to Graham's proposition, are called *colloïds*. The same hypothesis, in the most natural manner, leads us to the view already pronounced by our eminent colleague, Pflüger, that such a cumulation of molecules may extend further yet, and thus build up the form-elements of *living* organisms. Of these mass-molecules we may perhaps suppose further, that they through the constant change of position of polyvalent atoms show a constant change in the connected individual molecules, so that the whole—of course under generation of electricity—is in a sort of living state, particularly as, through identical changes of position, adjacent molecules may be drawn into the circle of combination and newly formed ones expelled."

The idea thus brought forward may perhaps be expressed by saying that, if ever chemists should succeed in obtaining albuminous bodies artificially, it will be in the state of living protoplasm, perhaps in the shape of those structureless beings which Häckel calls the *Monera*.

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* Nature, XVIII., 210.

All attempts hitherto made for the purpose of producing spontaneous generation have necessarily failed. The enigma of life can only be solved by the discovery of the synthesis of an albuminous compound.

The progress of organic chemistry has been so rapid, and the field which it covers so large, that it has been found necessary to have separate chairs for the inorganic and organic part of our science. How rapidly organic chemistry has developed may be seen from the fact that forty years ago the number of known hydrocarbons was about 12, and most of them were but very imperfectly known. To-day we are acquainted with at least 200, and many of these have been very carefully studied. What would Gmelin say now, who, in 1827, when writing his hand-book, requested organic chemists to stop, or else he should never finish! How the material has since increased and is still on the increase will be perhaps best shown by the fact that in the third supplement of Watts' Dictionary, which gives the progress which Chemistry has made from 1872 to the end of 1877, including some of the more important discoveries which appeared in 1878, the article on benzene and its derivatives occupies 100 pages; while in the second supplement, which brings the record of chemical discoveries from 1869 to the end of 1872, but included also some made in 1873 and 1874, the same subject is treated in 23 pages. Yet, in some respects, the subject is to-day more easily mastered than it could have been or was a few years ago. The large number of well ascertained facts have given rise to a more complete and simple systematisation. Compare a modern handbook with one published twenty years ago, or even some years later. How short are now these formerly so lengthy chapters treating of chromogens, colouring matters, indifferent crystalline compounds, bitter principles, essential oils, and other such bodies of unknown constitution which are found in plants and animals. Some of these groups have even entirely disappeared.

If to-day such bodies are discovered they may have an interest for the pharmaceutical or technical chemist, but as long as their constitution remains unknown, or at least until efforts have been made to ascertain it and bring the compound into some connection with a well defined group, the theoretical chemist takes hardly any notice of them.

We will close this short and imperfect sketch with some words of Hermann Kopp,* the great historian of chemistry, to whom this little work is dedicated:

"To none is it allowed to enjoy for long the progress of science and the results which future may bring to light. The alchemists of past centuries endeavoured to prepare the elixir of life, a means by which man might be kept healthy in body and mind for an unlimited space of time.

"We will not discuss here the question how far this might have been a benefit to the individual or not, nor whether it might have been an advantage for science if eminent men would have continued their researches for an unlimited period.

"The alchemists worked in vain; it is not in our power to appropriate to ourselves the experiences and results which future alone can bring. But in a certain sense we are indeed enabled to prolong our life backwards into the past by appropriating the experiences of those who were before us, and by becoming acquainted with their views so thoroughly as if we had been their contemporaries. The means of doing this is also an elixir of life. May the present attempt to contribute to this end be judged with indulgence."

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* Preface to "Die Entwicklung der Chemie in der neueren Zeit."

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